Ambipolar Charge Storage in Type-I Core/Shell Semiconductor Quantum Dots toward Optoelectronic Transistor-Based Memories

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Efficient charge storage media play a pivotal role in transistor-based memories and thus are under intense research. In this work, the charge storage ability of type-I InP/ZnS core/shell quantum dots is well revealed through studying a pentacene-based organic transistor with the quantum dots (QDs) integrated. The quantum well-like energy band structure enables the QDs to directly confine either holes or electrons in the core, signifying a dielectric layer-free nonvolatile memory. Especially, the QDs in this device can be charged by electrons using light illumination as the exclusive method. The electron charging process is ascribed to the photoexcitation process in the InP-core and the hot holes induced. The QDs layer demonstrates an electron storage density of $\approx 5.0 \times 10^{11}$ cm$^{-2}$ and a hole storage density of $\approx 6.4 \times 10^{11}$ cm$^{-2}$. Resultingly, the output device shows a fast response speed to gate voltage (10 µs), large memory window (42 V), good retention (>4.0 $\times 10^4$ s), and reliable endurance. This work suggests that the core/shell quantum dot as a kind of charge storage medium is of great promise for optoelectronic memories.

1. Introduction

Novel nonvolatile memory devices, such as memristors, phase-change memories, ferroelectric memories, floating-gate memories, etc., are going through a research upsurge as a response to the eager demand for a solution addressing the “Memory wall” in the modern silicon-based computing system. Thereinto, transistor-based memories (TBMs) are regarded as an important approach with unique advantages including nondestructive reading, modern integrated circuit architectural compatibility, and reliable switching characteristic. TBMs have a relatively straightforward working mechanism, that is, modulation of the conductance of the active layer by the charge storage nearby. In a conventional floating-gate transistor memory, the charge storage is realized through a bulk conductor (floating-gate) isolated from the active layer by a dielectric layer. Aiming for a better TBM device, semiconductor nanocrystals have been investigated as effective alternatives to the bulk floating gate, given that their abundant surface states render their charge storage ability huge, and discrete feature ensures a limited charge leakage. TBMs using nanocrystals of Si, CdSe, graphene, carbon, CsPbBr$_3$, CdSe/ZnS core/shell, etc. as the floating gates demonstrated outstanding figures of merits in terms of speed, endurance, retention, and so on. Meanwhile, thanks to the excellent optoelectronic property of the semiconductor nanocrystals, some output TBMs were endowed with optoelectronic operation ability, that is, the devices could be programmed and/or erased by the light illumination. Using a light as an operation method of TBMs has advantages including nondestructive operation, multiple data storage, etc. Moreover, these optoelectronic memories are of particular significance to the emerging all-optical circuit and sensory neuromorphic computing.

Nevertheless, most reports on optoelectronic TBMs based on semiconductor crystals are using the conventional floating-gate structure. Charges must travel across a dielectric layer to exchange between the charge storage medium and the active layer, which would hinder the speed, efficiency, and endurance of the device. In this regard, optoelectronic TBMs without the dielectric layer emerged. In relevant research, one well-known strategy for charge storage is to take advantage of trap states in either the active layer or the charge storage media.
Alternatively, structure-engineering of colloidal nanomaterials, namely, capping individual nano-charge storage media with charge blocking layer, have been proved to be another effective way for charge storage.[7,9,24,25] To illustrate, Jeon et al. reported that CdSe quantum dots (QDs) capped with selected surface ligands could be applied as effective charge storage media in a dielectric layer free optoelectronic TBM.[9] The device demonstrated a fast photo-induced erasing process due to the efficient charge exchange between the CdSe QDs and the active layer. Previously we have shown that colloidal type-I core/shell QDs could robustly store charges using its quantum well-like energy band structure. The charge injection/expelling would happen under a voltage bias. Resultingly, a dielectric layer free TBM with electrical operationality was fabricated.[25] Nevertheless, the application potential of the core/shell QDs in TBM is yet to be exhausted since the optoelectronic property of the material was not referred to. In this study, InP/ZnS core/shell QDs are used to address this issue. The QDs are put atop the active layer of a bottom-gate-configuration organic transistor based on pentacene. The type-I band structure of the core/shell QDs enables them to store both holes and electrons. The p-type pentacene is nailed down to be the hole supplier, which would inject the holes to the QDs through a diffusion process under a negative gate voltage. On the other hand, light illumination is found to generate electrons in the QD and thus be the only valid method to charge the QDs with electrons in this device. As a result, the device behaves as a good optoelectronic TBM that can be optically programmed and electrically erased. The state of the device can be well controlled by the electrical pulse power and the incident light dose, signifying an application potential of photonic artificial synapses.

2. Results and Discussions

The InP/ZnS core/shell QDs were synthesized using a reported method.[26] An InP-core was first synthesized and then wrapped by the ZnS shell through a layer-by-layer growth process of Zn and S atoms. The high-angle annular dark-field imaging transmission electron microscope (HAADF-STEM) images of the QDs were acquired and shown in Figure 1a, b. The figures demonstrate obvious contrast between the core and shell, denoting an InP-core diameter of about 8 nm and a ZnS-shell thickness of about 3 nm (Figure 1b). Notice that the core/shell QD has an irregular shape, implying that the growth of the QDs is subject to the Stranski–Krastanov growth mechanism.[27,28] Although an island-like shell was grown due to the strain energy induced by the lattice mismatch between the core and shell materials, there is a continuous shell film formed in advance, guaranteeing the complete core/shell structure. The photoluminescence (PL) spectrum of the InP/ZnS QDs in Figure 1c shows an emission peak at 642 nm, further verifying the successful capping of the ZnS shell on the InP-core, since the bare InP QDs are not luminescent.[26,29] The absorbance spectrum of the QDs in Figure 1c demonstrates a first excitonic peak at 608 nm, which corresponds to a bandgap of about 1.9 eV, as revealed by the Tauc plot in the inset of Figure 1c. A TBM was fabricated using a bottom-gate-top-contact structure, as schematically shown in Figure 1d.
The active layer of the device was prepared through spin-coating the InP/ZnS QDs atop a pentacene film with a thickness of about 20 nm, forming a QD-pentacene bilayer film. The cross-section scanning electron microscope (SEM) image of the device was acquired and shown in Figure 1e, manifesting a total thickness of about 40 nm of the active layer. Considering the diameter of about 14 nm of the InP/ZnS QDs, it implies a quasi-single layer close-packed QDs on top of the pentacene. The SEM image of the bilayer film in Figure 1f confirms the uniform distribution of the QDs on the pentacene, while the pure pentacene film has a smooth surface as shown in Figure S1a, Supporting Information. Moreover, cracks were found in the bilayer film after the deposition of the InP/ZnS QDs, which are ascribed to the damages induced by the spin-coating process of the toluene solution of QDs. The damages include the dissolution of pentacene induced by the toluene and the impediment to the pentacene crystallization during the post annealing process induced by the implanted QDs.

The transfer characteristics of the TBM device based on the QD-pentacene bilayer was measured in different regards with a $V_{DS}$ of $-30$ V. Figure 2a shows the cyclic transfer curves of the device with different $V_G$ sweep ranges. From top to bottom, the three characteristics were separately acquired with the device in the dark, under light illumination of 405 and 637 nm. The irradiances of the 405 and 637 nm lights were 3.7 and 9.1 mW cm$^{-2}$, respectively. $V_{DS}$ was set to be $-30$ V for all measurements; b) The curves of $V_{th}$ of the transfer curves in (a) versus the $V_G$ sweep ranges; c) Unidirectional forward transfer curves after bias or illumination operation were applied to the device. Operations ①, ②, and ③ were conducted successively, $V_{DS} = -30$ V; d) Schematics of the charge storage situations in the O-state and E-state in (c); e) Normalized $V_{th}$ of the E-state and O-state transfer curves along with time. The freshly attained E-state is deemed as 100% and O-state as 0; f) $V_{th}$ monitored while switching the TBM between the O-state and E-state more than 100 times.
in the QD-pentacene device, the pentacene film is in charge of charge conducting, and the QD film plays the role of charge storage medium. And the latter is responsible for the hysteresis of the transfer curves. The clockwise hysteresis of the transfer curve is typical in TBM, which is the sign of holes storage under negative $V_G$ and electrons storage under positive $V_G$. Nevertheless, there are some notable features in Figure 2a. For all three conditions, the backward curves leftward shift along with the increase of the $V_G$ sweep range, which is indicative of the increase of the stored holes. In the dark, the forward curves shift leftward with the increase of the $V_G$ sweep range as well, which is opposite to the knowledge that the positive $V_G$ would neutralize the stored holes or induce the electron storage. Moreover, each forward curve in the dark is almost at the same position as the previous backward curve, and the misalignment between each forward curve and its previous backward curve increases with the increase of the $V_G$ sweep range. It suggests that the positive $V_G$ is seriously incompetent to neutralize the stored holes induced by the negative $V_G$ with the same intensity while the incompetence keeps being alleviated with the increase of the stored holes. As a comparison, the transfer characteristics under light illumination show that this incompetence could be largely relieved by the illumination of 637 nm and eliminated by 405 nm. Namely, each forward curve under the 637 nm condition is in the right of the last backward curve, and all the forward curves under the 405 nm condition are in the same initial position. The threshold voltages ($V_{th}$) of the transfer curves in Figure 2a were extracted and plotted along with the $V_G$ sweep ranges in Figure 2b to exhibit the position change of the transfer curves. The results show clearly that the neutralization of the holes stored in QDs is efficient under the illumination of 405 nm, less efficient under 637 nm, and least in the dark. Under the 405 nm illumination, the cyclic transfer curve within $V_G$ of ±60 V produces the largest memory windows of about 42 V.

The memory windows signify the potential of the device to be applied as a TBM. The impacts of the electric bias and light illumination on the device were ascertained by studying the unidirectional forward transfer curves. The initial transfer curve with a $V_G$ of −13.1 V was first acquired and shown as the dashed line in Figure 2c. Then the light of 405 nm with the irradiance of 3.7 mW cm$^{-2}$ was used to illuminate the device for 150 s, and thus cast a total 2.2 mJ power (405 nm/2.2 mJ) to the channel area. The resulting transfer curve was found rightwards shifted to the position with a $V_{th}$ of −6.1 V. The optically induced state of the device is marked as the O-state from now on. After that, a $V_G$ pulse with an amplitude of −40 V and width of 100 ms (−40 V/100 ms) was applied to the device. Consequently, the transfer curve shifted to the left of the initial state, with a $V_{th}$ of −22.0 V. The electrically induced state is hereinafter marked as the E-state for short.

Again, light illumination (405 nm/2.2 mJ) was applied to the device in the E-state. As a result, the transfer curve went back to the previous O-state. The initial transfer curve reflects a state that no charge is stored in the QDs. The rightwards shifted transfer curves, that is, the O-state, corresponds to the electron storage in the QDs. Oppositely, the E-state points to the hole storage in the QDs. The charge storage situations in the O-state and E-state are illustrated in Figure 2d. The density of the stored charge ($n$) could be estimated through the equation: $n = \Delta V_{th} C_{SiO2} / \epsilon$, where $\Delta V_{th}$ is the $V_{th}$ change from the initial state, $\epsilon$ is the capacitance per unit area of the SiO$_2$, dielectric layer. The hole density ($n_h$) in the E-state and electron density ($n_e$) in the O-state were calculated to be $6.4 \times 10^{11}$ cm$^{-2}$ and $5.0 \times 10^{11}$ cm$^{-2}$, respectively. Furthermore, the QD density was evaluated to be about $3.9 \times 10^{11}$ cm$^{-2}$ through an SEM image shown in Figure S1f, Supporting Information. The charges stored in each QD are thus calculated to be about 1.6 for hole and 1.3 for electron. Hence, there are both singly and multiply charged QDs in the O and E-states, implying the possibility to further charge the QDs by increasing the bias voltage intensity or light irradiance. It is worthy of noting that the light illumination of 405 nm/2.2 mJ shifted both the initial and E-state transfer curves to the same O-state. It implies an upper limit of the electrons that can be stored in the QDs (5.0 $\times$ 10$^{11}$ cm$^{-2}$) under the current light irradiance of 3.7 mW cm$^{-2}$, and 405 nm/2.2 mJ is far more than the dose needed to reach the limit from the initial state. During the above measurement, the initial state was hard to fix since any bias or light illumination would induce the change of the device state. Therefore, the O-state with saturated electron storage was used as the benchmark of the device state. From the O-state, a $V_G$ of −40 V/100 ms would neutralize the stored electrons and then induced hole storage in the QDs. The nonvolatility of the charge storage in the QDs was characterized by monitoring the $V_{th}$ of the transfer curves in the E-state and O-state along with time, with the freshly attained E-state deemed as 100% and O-state as 0. The result in Figure 2f shows that the $V_{th}$ of the E-state and O-state converge to the initial state, indicating the release process of the stored charges. This release is slow, with over 60% of $V_{th}$ discrepancy retained after 4 × 10$^4$ s. Extrapolating to 10 years, there is still over 30% charges residual in the QDs. The retention performance could be improved by increasing the shell thickness and deliberately choosing the surface ligand of the QDs. Then the endurance of the QDs to the charging process was tested by repeating the hole charging (h-charging)/electron charging (e-charging) cycle 100 times. The h-charging was realized using a $V_G$ pulse of −40 V/100 ms, and the e-charging using a light illumination of 405 nm/2.2 mJ. The $V_{th}$ of the E-state and O-state transfer curves were extracted and shown in Figure 2e, demonstrating a stable endurance of the QDs in this test.

To ascertain the e-charging process clearly, different incident light doses of 405 nm were applied to the E-state device in Figure 2c. The induced transfer curves were acquired and shown in Figure S2a, Supporting Information. As expected, the number of the electrons charged into the QDs depends on the incident light dose, and from the E-state, a light power of 1.5 mJ is sufficient to charge the QDs with electrons of the upper limit number under the current light irradiance. Reversely, the h-charging process can be precisely controlled by the amplitude or width of the $V_G$ pulse as well. Figure S2b,c, Supporting Information, show the leftward shifts of the transfer curves from the O-state upon $V_G$ pulses of −40 V with variable width and $V_G$ pulses of 100 ms with variable amplitude, respectively. Figure 3a summarizes the dependence of the $V_{th}$ on the width of the $V_G$ of −40 V in an h-charging process from the O-state and the dependence of the $V_{th}$ on the incident dose of light illumination of 405 nm in the subsequent e-charging process from the E-state. A distinguishable $\Delta V_{th}$ was attained by a $V_G$ pulse with a narrow width of 10 µs, manifesting the
Figure 3. a) Dependence of the $V_{th}$ on the width of the $V_G$ of $-40 \text{ V}$ in an h-charging process from the O-state and on the incident dose of light illumination of 405 nm in the subsequent e-charging process from the E-state; b) $\Delta V_{th}$ ratio in the e-charging process from the E-state along with the incident photon numbers for different light sources. The $\Delta V_{th}$ between the O-state and E-state is regarded as 1; c) Absorbance spectra of the active layer of the device before and after the deposition of the QDs; d) Curves of $\Delta V_{th}$ versus incident light dose of 405 nm in e-charging processes that started from two different device states. One state is that a $V_G$ of $-40 \text{ V/100 ms}$ was applied to the device at the O-state; the other is that a $V_G$ of $-40 \text{ V/10 ms}$ was applied to the device at the O-state; e) Schematic of the h-charging process under a negative $V_G$; f) Schematic of the e-charging process under an illumination. The red carriers are the photo-induced hot carriers.

application potential of the core–shell QDs in fast speed memories.[20,21] It is worthy of pointing out that while $-40 \text{ V/100 ms}$ was used as the strongest h-charging operation, further increase of the $V_G$ amplitude or width would induce a larger leftward shift of the transfer curves, indicating for a huge hole accommodation ability of the QDs. Nevertheless, a further leftward shift of the transfer curve beyond the E-state of $-40 \text{ V/100 ms}$ made $V_{th}$ difficult to determine in the $V_G$ sweep range of $\pm 30 \text{ V}$, yet a wider $V_G$ sweep range would disorder the transfer characteristic by bringing out an unexpected h-charging effect. Therefore, $-40 \text{ V/100 ms}$ was chosen as the most intensive h-charging operation in the study on transfer characteristics. Compared with the straightforward electrically induced h-charging process,[9,13,31] the optically induced e-charging process needs to be addressed better since both the pentacene and QDs are light sensitive. To do so, light illuminations of 637 nm with different incident doses were used to charge the QDs with electrons, with the resulting transfer curves recorded and shown in Figure S2d, Supporting Information. As can be seen, a much larger light dose of 10.9 mJ of 637 nm than the 1.5 mJ of 405 nm was needed to saturate the QDs with electrons from the E-state. On the basis of Figure S2a,d, Supporting Information, the normalized $\Delta V_{th}$ were plotted along with the incident photon numbers in Figure 3b, with the $\Delta V_{th}$ between the O-state and E-state regarded as 1. The 405 nm light shows a much larger efficiency than 637 nm to charge the QDs with electrons. To explore the reason, the absorbance spectra of the active layer of the device before and after the deposition of the QDs are shown in Figure 3c, with the 405 and 637 nm located. It suggests that the absorption of the QD-pentacene film at 405 nm comes from the QD component mostly, and the absorption at 637 nm mainly comes from the pentacene component. Therefore, we infer that the photoexcitation in QDs makes the main contribution to the e-charging process. Considering the ZnS shell have a bandgap larger than 3.9 eV (bulk bandgap),[34] the photoexcitation shall only happen in the InP-core. Moreover, the e-charging processes started from different device states were compared to clarify the driving force for the charging. Two different h-charging operations, that is, $V_G$ of $-40 \text{ V/100 ms}$ or $-40 \text{ V/10 ms}$, were separately conducted to a device in the O-state. Then, 405 nm light was used to charge electrons into the device in these two different states. The induced $\Delta V_{th}$ were plotted along with the incident light dose in Figure 3d, demonstrating a smaller $\Delta V_{th}$ for the less h-charged state ($-40 \text{ V/10 ms}$) at the same light dose. It means that the e-charging speed is dependent on the charge density in the QDs.

Given the above, the scenario of the working process of the device was conceived and shown in Figure 3e,f. The InP/ZnS core/shell QDs have been widely revealed to have a quantum well-like type-I band structure.[26,34–36] The valence band and conduction band of the InP-core are estimated to be about 6.0 and 4.1 eV, respectively.[37] The pentacene has a valence band of 5.0 eV...
and a conduction band of 3.2 eV.\textsuperscript{[14]} The thin ZnS shell would have a very large bandgap due to the quantum confinement effect, with a conduction band above the pentacene and a valence band lower than InP-core.\textsuperscript{[36]} A negative $V_G$ leads to the accumulation of holes in the pentacene due to the capacitive coupling effect. The holes can overcome the energy barrier formed by the ZnS shell as well as the unfavorable valence band alignment between the pentacene and InP-core and get injected into the InP-core (Figure 3e). Since the QDs layer is placed atop the pentacene, no bias is supposed to be applied to the QDs during the bottom $V_G$ proceeding. Hence, the injection would be motivated only by the diffusion force formed due to the high concentration discrepancy between the QDs and pentacene. If there are electrons stored in the QDs in advance, they will be neutralized first. The ZnS shell with a lower valence band can confine the holes in the InP-core.\textsuperscript{[25]} On the other hand, when a light (405 or 637 nm) illuminates the device, photo-induced hot electrons and holes are generated in the InP-core. The holes would transfer to the pentacene, inducing an e-charging process in the QDs. The previously stored holes (if any) in the QDs would help accelerate the e-charging process, thanks to the increased hole concentration. As a contrast, Figure S3a,b, Supporting Information, show that a positive $V_G$ of 40 V cannot induce any change of the transfer curve from its initial state and O-state, respectively. The reason can be attributed to that the p-type pentacene can only play the role of a hole supplier,\textsuperscript{[9,31,33]} and a positive $V_G$ would deplete the holes in the pentacene film. Figure S3c, Supporting Information, demonstrates that the transfer curve in the E-state cannot be changed by a positive $V_G$ neither, meaning that a positive $V_G$ is incompetent to neutralize the stored holes in the QDs. This is accordant with the above analysis of Figure 2a. In principle, the depletion of holes in the pentacene under a positive $V_G$ would increase the hole concentration discrepancies between the QDs and pentacene. It seems that the diffusion force is not large enough to overcome the barrier between the InP-core and pentacene even though there is a favorable valence band alignment. Therefore, the diffusion force, the energy of the hot holes, and the favorable valence band alignment may all contribute to the e-charging process under illumination. Their exact roles need to be addressed further.

The channel currents ($I_{DS}$) of the transistor upon different charging processes were characterized to explore the performance of the device as a TBM. In all coming study, the $I_{DS}$ were read at $V_G$ of $-20$ V and $V_{DS}$ of 10 V. To eliminate the impact of the reading process on device state, the $I_{DS}$ reading was carried out at a fast sampling speed with only two sampling points. First, h-charging from the benchmark O-state was conducted to the device using $V_G$ pulses of $-40$ V with different widths. After each h-charging operation, the device was restored to the O-state using illumination of 405 nm/2.2 mJ. The $I_{DS}$ of the device after each h-charging and restoring were recorded and plotted along with the $V_G$ pulse width, as shown in Figure 4a. It demonstrates that a distinguishable $I_{DS}$ change can be made by a $V_G$ of $-40$ V/50 µs. The writing time at the sub-millisecond level is
consistent with the 10 µs obtained from the above $V_{th}$ characteristic (Figure 3a). In the same way, the dependence of the $I_{DS}$ after an e-charging operation on the incident light dose was acquired and shown in Figure 4b. After each e-charging operation, the $I_{DS}$ was restored to an off state using a $V_{G}$ of −40 V/500 ms, which was proved necessary to attain an off $I_{DS}$ in Figure 4a. As can be seen, the $I_{DS}$ becomes stable after 1.5 mJ light was cast to the device, and further illumination would not change the value, which corroborates the above discussion (Figure S2a, Supporting Information). The endurance and retention characteristics of the device were studied by conducting the most intensive h-charging ($V_{G}$ of −40 V/500 ms) and e-charging (405 nm/2.2 mJ) operations. Figure 4c shows the $I_{DS}$ recorded during 100 times successive operation cycles, suggesting a good endurance of the device. The decays of the $I_{DS}$ after h-charging and e-charging operation were separately recorded along with time and shown in Figure 4d. The $I_{DS}$ in two different states demonstrate a limited decay in $3 \times 10^4$ s, denoting the robust charge storage in the core/shell QDs. Some reported transistor-based memories using core/shell QDs as the charge storage media are summarized and compared with the presented one in Table 1. The presented device possesses a simpler structure without the tunneling dielectric layer, benefit from which it can be programmed by a narrower electrical pulse. Meanwhile, the presented device also has a benign information retention performance and optical operability. The potential of the TBM in the construction of an artificial neuromorphic system has been widely revealed by using the devices to simulate the main synaptic functions. The optoelectronic TBM, which can respond to both electric and optical stimuli, possess two approaches to mimic the plasticity of a synapse. Figure 4e illustrates the correspondence between an actual synapse (left) and an artificial synapse (right) based on our device. In this regard, light spikes of 405 nm with an intensity of 14.8 µW and duration of 1 s were cast to the channel of the device with a frequency of 0.5 Hz, realizing a photonic potentiation of the artificial synapse. Then, electric spikes of $V_{G}$ with an amplitude of −40 V and width of 1 ms were applied to the device with an interval of 0.1 ms to conduct an electric depression. The result in Figure 4f shows that 200 excitatory light spikes and 1000 inhibitory electric spikes manage to achieve a potentiation-depression cycle in the device.

3. Conclusions

InP/ZnS core/shell QDs were implanted into an organic transistor based on pentacene, forming direct contact with the active layer. A battery of studies reveals the nonvolatile ambipolar charge storage ability of the QDs, which is ascribed to the type-I energy band structure that can confine both electrons and holes in the core. A negative gate voltage would accumulate holes in the semiconductor layer and induce hole diffusion to the QDs. The direct contact between the QDs and pentacene leads to a fast electron charging speed, which could establish a distinguishable $V_{th}$ change upon a $V_{G}$ pulse of −40 V with 10 µs width. On the other hand, the photoexcitation effect in the InP-core was proved to be exclusively responsible for the electron charging to the QDs. The electrically induced hole charging and optically induced electron charging properties of the QDs enable the device to be applied as a nonvolatile optoelectronic memory. The memory can be programmed by light and erased by negative $V_{G}$, demonstrating a memory window of up to 42 V, good retention in $4 \times 10^4$ s, and benign endurance. Based on this device, an artificial synapse with optical potentiation and electric depression functions was demonstrated. This work manifests the excellent advantages of the type-I core/shell QDs as charge storage media in nonvolatile optoelectronic memories.

4. Experimental Section

Materials Preparation: All materials and reagents for QD synthesis were purchased from Sigma-Aldrich and used as received without further purification. Pentacene for thermal evaporation was purchased from Xi’an Baolaiti Ltd. InP/ZnS core/shell QDs solution in toluene were synthesized using a reported method. Indium (III) chloride (100 mg, 0.45 mmol) and zinc (II) chloride (300 mg, 2.2 mmol) were mixed in oleylamine (5.0 mL). The mixture was degassed at 120 °C for an hour under stirring. The solution was then heated to 180 °C under an Argon atmosphere. Tris(diethylamino)phosphine (0.45 mL, 1.6 mmol) was quickly injected into the solution swiftly, so began the growth process of the InP nano-core. On the other hand, sulfur (S) powder was solved in Trioctylphosphine (TOP) to get the S precursor with a concentration of about 2.2 mol L$^{-1}$. At the 20th min of the growth process of the InP-core, 1 mL S precursor was injected into the solution. Since the 60th min, the temperature was increased to 200 °C.

### Table 1. Summary of concerned device features of some transistor-based memories using core/shell QDs as the charge storage media.

| Core/shell charge storage medium | Tunneling dielectric | Minimum electrical pulse width used [s] | Measured retention [s] | Optical operability | Ref. |
|---------------------------------|----------------------|----------------------------------------|------------------------|-------------------|-----|
| CdSe/ZnSe                       | None                 | 1.0                                    | $8 \times 10^4$        | Yes               | [45]|
| CdSe/ZnS                        | PMMA                 | 0.5                                    | $5 \times 10^3$        | No                | [46]|
| Au/GeO$_2$                      | SiO$_2$              | 1.0                                    | $1 \times 10^5$        | No                | [24]|
| CdSe/ZnS                        | Al$_2$O$_3$          | 1.0                                    | $1 \times 10^5$        | Yes               | [13]|
| CdSe/ZnS                        | Al$_2$O$_3$          | 10.0 µm                                | $1 \times 10^4$        | No                | [47]|
| CdSe/ZnS                        | Al$_2$O$_3$          | 10.0 µm                                | $1 \times 10^4$        | No                | [48]|
| Au/Pd                           | Al$_2$O$_3$          | 1.0 µm                                 | $1 \times 10^4$        | No                | [49]|
| Au/PS                           | PS                   | 2.0 µm                                 | $1 \times 10^4$        | No                | [50]|
| CdSe/ZnS                        | Al$_2$O$_3$          | 10.0 µm                                | $1 \times 10^4$        | Yes               | [51]|
| ZnSe/ZnS                        | None                 | 0.1                                    | $4.1 \times 10^4$      | No                | [25]|
| InP/ZnS                         | None                 | 10.0 µm                                | $4 \times 10^4$        | Yes               | This work |
At the 120th min, 4 mL Zn precursor was injected into the solution. Then the temperature was increased to 220 °C. At the 150th min, 0.7 mL S precursor was injected, then the temperature was increased to 240 °C. At the 180th min, 2 mL Zn precursor was injected, then the temperature was increased to 260 °C. At the 210th min, the temperature was cooled down to room temperature. The synthesized InP/ZnS QDs were then precipitated by adding ethanol and the following centrifugation. The supernatant was discarded. The precipitation was dissolved in toluene. This process was repeated once. The final solution was ready to use then.

**Device Fabrication:** Si/SiO2 wafer with heavily p-doping Si and SiO2 of 300 nm thickness was used as the substrate. P-type pentacene film with a thickness of 20 nm was thermally evaporated on the cleaned substrate as a semiconductor channel. 50 nm Au electrodes were deposited as the source and drain electrodes on the surface of the film by thermal evaporation through a shadow mask defining a length/width of 0.2/2 mm. Then in a glovebox filled with nitrogen, 5 mg mL⁻¹ InP@ZnS QDs solution was spin-coated at a speed/duration of 2000 rpm/60 s on the top of the semiconductor layer. The film was then annealed at 60 °C for 30 min.

**Characterizations:** High-angle annular dark-field imaging scanning transmission electron microscope (HAAADF-STEM) images were acquired on an FEI Titan Cubed Themis G201 double spherical aberration-corrected transmission electron microscope with an acceleration voltage of 300 kV. Absorbance spectra were measured using a GBC Chintra2020 spectrometer with tunable wavelengths. Photoluminescence (PL) spectra were obtained on a Fluorescence Spectrometer (Edinburgh instruments). Scanning electron microscope (SEM) images were obtained using a HITACHI SU8010 scanning electron microscope. Electrical characteristics of the transistors were measured using the combination of a Keithley 4200SCS parameter analyzer and a probe station. CHI continuous lasers with wavelengths of 405 nm and 637 nm were used for the relevant experiments. The electrical and optical measurements conducted on the devices were carried out in a glovebox filled with nitrogen.

**Statistical Analysis:** 19 TBMIs with identical channel area of 0.4 mm² were fabricated and characterized for their transfer characteristics in Figure 2a. They demonstrated the same feature with diverse exact values. Thus, a representative device was used to carry out the systematical characterization. The data for Figure 4a,b,c,f were presented as the mean ± standard error using the raw data from one time measurement of the same device. The calculation of the standard error was carried out using the embedded function in the Excel (Office 365, Microsoft Corporation, USA). The normalization processing was conducted using the normalization function of the Origin8 software (OriginLab Corporation, Northampton, USA). All Graphical presentations were performed by the Origin8 software.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

InP/ZnS quantum dots, optoelectronic memory, organic transistors, photonic synaptic transistors, type-I core–shell quantum dots

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