Electrical/optical dual-function redox potential transistor

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We demonstrate a new type of transistors, the electrical/optical “dual-function redox-potential transistors”, which is solution processable and environmentally stable. This device consists of vertically stacked electrodes that act as gate, emitter and collector. It can perform as a normal transistor, whilst one electrode which is sensitised by dye enables to generate photocurrent when illuminated. Solution processable oxide-nanoparticles were used to form various functional layers, which allow an electrolyte to penetrate through and, consequently, the current between emitter and collector can be controlled by the gate potential modulated distribution of ions. The result here shows that the device performs with high ON-current under low driving voltage (<1V), while the transistor performance can readily be controlled by photo-illumination. Such device with combined optical and electrical functionalities allows single device to perform the tasks that are usually done by a circuit/system with multiple optical and electrical components, and it is promising for various applications.

Transistor, one of the most important inventions in the 20th century, has always been a research focus in both the academia and industry. Research concerning transistors has been very active in several domains. Significant efforts have been provided exploring new functional materials like inorganic crystalline semiconductors1–5, small molecule and polymer semiconductors6–11, nanotubes12,13 and recently graphenes14,15. The revolutionary achievements of transistors can also be attributed to the adoption of novel device architectures and operating principles, such as the application of field effect16,17, dynamically doping/dedoping18 etc. Low-cost fabrication based on solution process has also drawn considerable attention in the past decade6,11,19,20. Solution processable large-scaled organic transistor based circuit, with a great potential to reduce fabrication cost, has already been demonstrated21.

An important forefront of transistor research resides in the area of multi-functionality devices, which allow a single device to replace a circuit block of components in different domains such as electronics and optics. A reduction in the number of components will lead to increased system package density with increased functionality and consequently improved system performance. For example, a light emitting transistor which combines the functionalities of both a transistor and a light emitting diode (LED) is promising due to reduction of system complexity and cost in optical communication modules and electrically driven lasers22,23. Despite the significant progress made so far in this field, exploration of new types of transistors, novel materials and low cost manufacturing technologies is still continuing. Here we use solution processable oxide nanoparticles to realise a low cost and environmentally stable transistor in which the electrical current between two electrodes can be controlled by a third electrode through tuning redox process. Besides operating as a normal transistor (electrically controlled) the device can also respond to illumination as one of its electrodes is sensitised by dyes which converts photons into charge carriers.

Results

Figure 1 shows a schematic illustration of the proposed device structure (Fig. 1a), fabrication process (Fig. 1b) and transistor with common emitter configuration (Fig. 1c). The gate electrode is made of fluorine doped tin oxide (FTO) layer coated with a 30 ~ 50 nm thick bulk TiO2 film. To realize photo-response a layer of n-type semiconductor nanoparticles (TiO2) is deposited onto the FTO and sensitized with dyes. The porous emitter electrode is formed from indium tin oxide (ITO) nanoparticles in between the gate and collector electrodes (detailed in method section). A ZnO nanoparticle layer is used as a supporting layer to isolate the emitter from the Pt-catalyst coated FTO collector. Electrolyte is filled into the space between the gate and collector. Figures 2a and
2b show typical electrodes fabricated and Fig. 2c shows a scanning electron microscope (SEM) image of the ZnO and ITO films coated on FTO substrate where the colors generated by energy-dispersive X-ray (EDX) analysis represent the corresponding materials (Green: In, Pink: Zn, and Blue: Sn).

The devices were characterized using Keithley 2400 multimeters, an oscilloscope, and a xenon light source with adjustable light intensities.

Figure 1 | Schematic illustrations of (a) the proposed device architecture, (b) fabrication process, and (c) the device with common emitter configuration.

Figure 2 | Optical images of (a) the emitter/collector electrodes and (b) the gate/photo-electrode and (c) SEM image of the ZnO and ITO films coated on a FTO/glass substrate. The colors generated by EDX analysis represent the corresponding materials as: Green: In, Pink: Zn, Blue: Sn.

Figure 3 shows output curves of collector current-voltage ($I_C$-$V_C$) taken at various gate voltages ($V_G$) and transfer curves of $I_C$-$V_G$ under constant collector voltage (inset, $V_C = 0.8$ V). The measurement was done using a common emitter configuration (Fig. 1c) under dark (Fig. 3a) and illumination with 100Klux light (Fig. 3b). The obtained characteristics of our devices are rather similar to that of the well-developed triode (see supporting information, Fig. 1).
However the device we demonstrated here does not require a hot cathode, the drive voltage is two orders of magnitude lower, and can be easily miniaturized to micro-scale. The measured dark current of gate is less than \( 0.001 \text{ mA/cm}^2 \) which is the leakage current caused by the reduction of ions on the exposed FTO surface due to the imperfection of the thin bulk TiO₂ film. The small dark current of gate reveals that the device functions as a “field effect” or “redox potential effect” transistor. Currently achieved on/off current ratio of the transistor is \( 2 \times 10^{10} \) which can be further increased by improving the quality of the ZnO particle film. Data scattering from same batch of devices (6 devices per batch) is indicated on transfer curve in Fig. 3a for ON and OFF current. The scattering of ON-current is ~10%, but the data scattering of OFF-current can be several times which causes the overall scattering of the ON/OFF current ratio. The high ON-current of the devices is mainly attributed to the vertical channel architecture applied, and the drain current is much higher when the devices are illuminated by light. The architecture and principle of field control of the device are different from the standard field effect transistor, and hence the field effect mobility of the device cannot be extracted from existing formula. Mobility of ions in our devices was estimated to be \( -10^{-4} \text{ cm}^2/\text{V.S} \). The estimation is done according to the procedure described by Koneshan et al.²⁴ where mobility of ions, such as \( \Gamma \), in solutions was given. The device current is proportional to charge mobility, thus finding a new electrolyte with higher charge mobility is beneficial to improve the performance.

Functions that usually cannot be performed with normal transistors are anticipated with the transistor demonstrated here. For instance, a single such device can function as photo-enabled current switch which is generally realized by a multi-component circuit (photo-conductor + potential shift circuit, see supporting information, Fig. 2). Fig. 4c illustrates the principle of performing such a function. The difference of voltage shift of \( V_E \) lines (see Fig. 4c) under dark \( T_d \) and illumination condition \( T_l \) allows to identify a voltage \( \delta V_E \) under which two collector currents with equal current amplitude but opposite polarity are found. Figure 4d shows the current output under an applied \(-50 \text{ mV}\) bias to the emitter while a
mechanical shutter is used to block an illuminated light periodically. The reversing of current polarity with photo-illumination demonstrates the switching function of the device. From Fig. 4b, it shows that a linear relation is maintained for negative emitter voltage and current cutoff happens when the emitter voltage becomes positive. This unambiguously shows that the transistor characteristic in Fig. 3 is indeed originated from a nonlinear conductance behavior which is also the basis of many other important electronic devices like diode, triode, bipolar junction transistor etc. To further clarify this, a rectification function was demonstrated. Fig. 4e shows how an input sinusoidal signal can be rectified and Fig. 4f shows a typical half-wave rectification output obtained when a sinusoidal voltage signal is applied to the emitter with 0.2 V dc bias to the collector.

Discussion

The output curve with near exponential characteristics under a given gate voltage (see Fig. 3) can be qualitatively understood by the Tafel equation which describes variation of current density $i$ with applied potential $AV$ on an electrochemical system:

$$i = nFk \exp\left(\frac{znFAV}{RT}\right),$$

Where $n$ is the number of electrons involved in the electrode reaction, $F$ is the Faraday constant, $k$ is rate constant for electrode reaction, $R$ is universal gas constant, $z$ is charge transfer coefficient and $T_{\text{abs}}$ is absolute temperature. For small applied voltages a linear $I$-$V$ relation is maintained. The gating effect (transfer characteristics of transistor) can be explained by controlling ion blockage of reduction process in the porous electrode. The reduction at the porous electrode and oxidation process at the collector electrode can be described as:

$$I_s^- + 2e^- \rightarrow 3I^- \quad \text{(2.1)}$$

$$3I^- - 2e^- \rightarrow I_s^- \quad \text{(2.2)}$$

The gating process in the common emitter configuration is shown in Fig. 4g. When a positive voltage is applied to the collector while the gate voltage remains zero (left of Fig. 4g), the reduction of triiodide is largely prohibited by adsorption of potassium ions on emitter material surface due to the nature of positive charge of $K^+$. When a negative gate bias is applied (right of Fig. 4g) the $K^+$ drifted to gate from the emitter surface and the reduction of triiodide can take place through thermal diffusion. Thus, the device is switched-on by a negatively applied gate-voltage and behaves like a p-type transistor.

Previously there have been efforts to fabricate electronic devices by using electrochemical process. For instance Wang et al. have demonstrated phototransistors based on dye sensitized solar cell structure, however no electrically gating has been achieved. Although transistor that responds both electrically and optically has also been demonstrated previously, it was based on standard field effect transistor configuration which is fundamentally different from the work demonstrated here.

The emitter and collector electrodes have a low charge transfer resistance (to/from electrolyte). In contrast, the gate electrode has a higher charge transfer resistance which is realized by surface treatment with the thin bulk TiO$_2$ film and this ensures a minimization of gate current induced by reduction reaction on it. As the bulk TiO$_2$ film is too thin (30 – 50 nm) to hold high gate voltage, increasing gate modulation capacity requires a new device architecture where the synthesized TiO$_2$ can be fabricated on emitter electrode while an insulator film is deposited onto the gate. The device structure with

Figure 4 | (a), (b) Dark and photo-response of a transistor measured with common gate configuration (see inset of b) at Vc = 0 and 0.2 V, respectively; (c), (d) A schematic illustration of principle of performing as photo current-switcher and experimental result of this function. The red arrows indicate different current directions when the device performs with and without illumination; (e), (f) A schematic illustration of the input and output waveforms of the device, performing as rectifier and experimental result of this function; (g) A schematic illustration of proposed mechanism of emitter-collector current change with applied gate voltage.
stacked-layers allows a high drain current density and to avoid lithographically patterning of small lateral channels of transistors which in turn allows the use of current printing technology with ~10 μm resolution to fabricate transistors with micron size. Potentially there is a huge space to reduce the fabrication cost further. For normal function of transistor (electrically control only) the TiO2 particle film and dye application could be eliminated and the Pt layer can be replaced by much cheaper materials, like carbon. Here the basic principle of the device is demonstrated by a well-known electrolyte which could be replaced by other materials, like solid electrolyte, which enable further miniaturization of the devices and improvement of its performance and stability. Nanoparticle materials, like ZnO, can also be further developed or replaced to improve the ON/OFF current ratio (>10) and this can be done by using highly resistive, smaller sized (~5 nm) nanoparticle with better film forming property to avoid leakage induced by trapping of the subsequently coated conductive nanoparticle into the voids or defects. The lifespan of the fabricated devices should be similar to that of DSSC devices, and a typical DSSC life-time is estimated to be longer than 15 years under harsh out-door condition14. In addition, the devices demonstrated here have further proven the potentials of nanomaterial-based electrical/optical devices13–15.

Methods

A PTO film casted on glass substrate was pattern by wet etching using 2 M HCl aqueous solution with assistance of zinc powder to define a “U” shaped gap to isolate the collector and contact pad of the emitter (Fig. 1b(ii)). Then, Pt catalyst precursor (Platsol, Solaronix) was drop-casted onto the structured substrate and dried for 10 min at ambient condition and subsequently annealed at 450 °C for 30 min to convert the precursor to Pt catalyst. Then a 1.5 μm thick ZnO film was formed by spin-coating from its water based nanoparticle (~35 nm) suspension onto the Pt coated film at 100 °C for 10 min (Fig. 1b(iii)). Next, a 4 μm thick ITO film was deposited by spin-coating from isopropanol based colloidal suspension (~50 nm) and baked at 150 °C for 30 min (Fig. 1b(iv)). For the preparation of the photosensitive electrode (also gate) oxygen plasma cleaned FTO/glass substrate was treated in 0.05 mol TiCl4 aqueous solution for 1 hour at 80 °C to form 30 ~ 50 nm thick amorphous TiO2 film and the film was crystallized at 450 °C for 30 min. TiO2 nanoparticle (15 ~ 20 nm) paste/suspension is deposited on the FTO substrate by screen-printing and baked at 120 °C for 10 min to produce a 6 μm thick TiO2 nano-particle film (Fig. 1b(i)). The lateral dimensions of oxide films used here were defined by adhesion type masks with windows of dimensions of 8 mm x 10 mm (ZnO), 10 mm x 8 mm (ITO), and 6 mm x 6 mm (TiO2) respectively. After calcinations of these oxide films at 450 °C for 30 min, the TiO2 particle film was submerged into cis-disiooxantohinobilio-2,2',3,4',5,6,7,8-octahydrochalcone (N719) dye solution [0.3 mM in acetonitrile + tert-butanol (1:1)] for 12 hours and then rinsed using acetonitrile. After bonding the gate and emitter/collector electrodes with a 60 μm thick hotmelt film at 100 °C (Fig. 1b(iii)) an acetonitrile-based electrolyte that contains 1/3,1/3 redox couple (0.5 M KI, 0.05 M I2 in acetonitrile) is introduced through predrilled holes (Fig. 2a) and the device is sealed using the hotmelt film.

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Author contributions

S.L. conceived and designed the research. S.L. W.W. and J.X. have conducted device fabrication and test. Z.J.S., D.C., S.R. have contributed to experiment design and result analysis. S.L. and S.R. involved funding application and wrote the paper with the help of all others.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

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