A flexible integrated photodetector system driven by on-chip microsupercapacitors

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Abstract
Flexible multi-functional nano/micro-systems with integrated energy units and functional sensing/detecting units on a single chip have gained considerable attention recently due to their optimized maximum functionality within a minimized sized chip and excellent mechanical flexibility and stability. In this work, we present a prototype of a flexible integrated on-chip photodetecting system with a reduced graphene oxide (rGO)-based in-plane microsupercapacitor and a CdS nanowire-based photodetector. For the system, the optimized electrodes in the microsupercapacitor were utilized as the source and drain electrodes of the CdS photodetector simultaneously, configuring a minimized self-powered-like visible light photodetector system without external power source. Driven by the microsupercapacitor (volumetric capacitance = 8.01 F/cm³ and energy density = 6.204 Wh/cm³), current on/off ratios of 34.50 and 79.81 were obtained for the CdS-based photodetector depending on the number of the microsupercapacitors. The performance of the designed systems exhibited stable photo-current response consistent with the conventional one driven by the external power source, demonstrating the feasibility of the flexible integrated photodetector systems, which are promising for further large-scale and integrated applications.

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Introduction

Compared with traditional single-effect electronics, multi-functional integrated nano/micro-systems have achieved more concentration attributed to the multi-functional effect within the smallest volume [1]. Multi-functional integrated nano/micro-system is a complete system that consists of both energy harvesting and storage units and the functional sensing/detecting or other functional components, aiming at building a self-powered system that operates independently, sustainably and wirelessly by itself without any external battery, also called the “self-powered nanosystem”[1b].

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Taking advantage of highly integration, this nanosystem exhibits the merits of small volume, light weight and multifunctions. During the past 10 years, the self-powered systems built on the energy harvesting and energy storage systems have been widely studied and different kinds of integrated systems have been successfully designed such as the integrated solar cell and lithium battery systems, solar cell and supercapacitor systems, nanogenerator and supercapacitor system etc [2]. Although a few reports about the integrated systems built on the energy storage and sensors have been reported by our group, the traditional stacked energy storage devices in the reported systems limited the space reduction of the whole system [3].

Recently, on-chip micro-energy storage devices are becoming a research hot due to the fast progress and special demanding of microelectronics [1c,4]. Among them, micro-supercapacitors (mSCs) with high power density, fast charge-discharge ability, infinite cycle life and intrinsic safety are suitable for the energy storage and power source for micro-electronic device and the tuned filter in integration circuit [1c,1d,5]. The shorter ion diffusion path in microsupercapacitor (mSC) results in a higher power density compared with the traditional supercapacitor [6]. Meanwhile, novel mSCs with in-planar interdigital structure would buffer the deformation stress in the flexible devices [7]. Graphene is one of the popular electrode materials utilized in the mSCs for its excellent conductivity, film-forming ability and favorable mechanical property [1d,8]. Till now, several kinds of methods have been explored for manufacturing flexible mSCs, such as laser-scribing method and electrochemical depositing method etc. [1d,1g]. Compared with those methods, the UV photolithography technology combined with plasma etching method seems to be a much simpler and efficient way, which can efficiently couple micro-energy storage device with other nano-devices such as nano photo-detectors on a single chip to form compact integrated on-chip micro/nanosystems [9].

In this work, combining the micro-manufacturing technology of flexible mSC and photodetector, we designed a prototype of a self-driven on-chip photodetector system by integrating an rGO-based in-plane mSC with a CdS nanowire-based photodetector. The optimized electrodes in the mSC device were utilized as the source and drain electrodes of CdS photodetector as well, configuring a self-powered visible light photodetector without external power source. Moreover, the bias voltage of the photodetector can be tuned by scaling up the individual mSC system to a tandem system. The current on/off ratios were obtained by the individual and tandem microdevices respectively, exhibiting a photo-current response consistent with the one driven by the external power source.

**Experimental section**

**Preparation of reduced graphene oxide (rGO) mSC**

The fabrication process of the rGO mSC is exhibited in Figure 1. Firstly, PET substrates (2 cm × 3 cm) were cleaned by acetone, ethanol and distilled water in sequence. To enhance the hydrophilicity of PET, the top side of the PET substrate was treated by oxygen plasma (750 V, 20 min) in plasma cleaner with 0.6 L/min of air flow. Then, 1 mL of dispersed graphite oxide (GO) solution (1 mg/mL) was dropped onto the surface. GO sheets were synthesized by a modified Hummer method using natural graphite powder [10]. After being dried at room temperature overnight, a uniform GO film was formed on the PET substrate. Subsequently, photoresist was spin-coated on the GO film at 500 rpm for 15 s and 4000 rpm for 30 s. After spinning coating for three times, the substrates were heated at 100 °C for 4 min and the resist was subsequently patterned to obtain the desired surface structures on the GO film using the ultraviolet lithography machine with the mask and developed for 20 s. Then, oxygen plasma treatment (750 V, 80 min) was applied to etch the exposed GO in the plasma cleaner with 0.6 L/min of air flow. After removing the extra resist, patterned GO film was obtained. Hydrazine vapor was used to reduce GO pattern into rGO pattern at room temperature for 24 h. To improve the electrical contact between the square electrodes in the pattern with testing probes, the electrodes were evaporated with 20 nm Au. Furthermore, a clear gel electrolyte composed of 3 g of KOH, 6 g of polyvinyl alcohol (PVA) and 60 mL H2O prepared at 100 °C under 2 h stirring was spread on the integrated electrodes of the microsupercapacitor. After vaporizing the excess water, an all-solid-state rGO micro-supercapacitor was obtained.

![Figure 1](image-url)

**Figure 1** Schematic illustration of the fabrication process of the flexible microsupercapacitor made up of 20 fingers integrated on the PET substrate. The fabrication process flow includes spreading GO dispersion on the PET substrate, photolithography of the pattern, air plasma etching of the extra GO, removing the resist, hydrazing reduction of GO, sputtering Au on the electrodes and coating gel electrolyte.
Fabrication of CdS nanowires

CdS nanowires were synthesized via a CVD method. Firstly, 0.06 g of CdS powder was placed in the center heating zone of the furnace. Then Si wafer with gold particle used catalyst on the surface was placed in the downstream position nearly 16 cm away from the center. The furnace was first pumped with pure N₂ 30 min to clean the remaining air before heating. Then the furnace was heated into 950 °C in 30 min and maintained at this temperature for 0.5 h. High purity N₂ at a constant flow rate of 100 sccm (standard cubic centimeters per minute) was put in as the protecting medium and carrier gas. After reaction, the furnace was cooled into room temperature naturally. Then a yellow wool-like product was found on the Si slice.

Fabrication of CdS nanowire photodetector on the rGO microsupercapacitor

After the CdS nanowires being removed from the Si slice, 10 μL of CdS solution (20 mg/mL in isopropanol) was spread in one of the gaps between the square electrodes. Nanowires formed a dense film connecting the middle electrode and one of the electrodes of microsupercapacitor. After drying, the device was available for testing.

Characterization and measurement

The thickness of the rGO patterns was measured by a laser scanning confocal microscope (VK-9700, KEYENCE). X-ray photoelectron spectrometer (GENESIS, America's dax co., LTD). The energy storage properties of microsupercapacitor were measured by the CHI (760D) electrochemical work stations. The photoelectric properties of the photodetector were measured by the Keithley semiconductor characteristics analysis system.

Calculations

The capacitance (C) of the supercapacitor is calculated from the CV curves at different scan rates using the formula:

\[
C = \left( \int idV \right)/\nu(\Delta V)
\]

where \(i\) (in amps, A) is the response current, \(\nu\) is the potential scan rate (V/s) and \(\Delta V\) is the applied potential region (in volts, V).

The capacitance (C) of the supercapacitor calculated from the galvanostatic charge-discharge curves at different current densities is using the formula:

\[
C = i/(-dV/dt)
\]

where \(i\) (in amps, A) is the applied current, \(dV/dt\) is the slope of the discharge curve (in volts per second, V/s).

The areal capacitance and volume capacitance of the microsupercapacitor are calculated according to the following formula respectively:

\[
C_A = C/A
\]

\[
C_V = C/V
\]

where \(A\) and \(V\) refer to the area (cm²) and volume (cm³) of the interdigital electrodes in microsupercapacitor respectively.

The voltage energy density (\(E\)) in W h/cm³ and power density (\(P\)) in W/cm³ derived from galvanostatic charge-discharge curves are calculated from the following expressions:

\[
E = C(\Delta E)^2/(2V \times 3600)
\]

where \(\Delta E\) is the operating voltage window (measured in volts and obtained from the discharge curve excluding the voltage drop);

\[
P = \Delta E^2/(4RV)
\]

where \(R = (V_{drop}/2i)\) is the internal resistance of the device that is estimated from the voltage drop \((V_{drop})\) at the beginning of the discharge curve.

Results and discussion

Flexible on-chip rGO based mSC used in the integrated system was fabricated via a conventional ultra-violet lithography process and the corresponding fabrication process was depicted in Figure 1. To produce a uniform graphene oxide (GO) film, before spreading the GO dispersion, PET substrate was treated by air plasma to enable good wettability of the water based GO dispersion [5]. Then, through a conventional lithography process, the photore sist covered micro-pattern of the mSC with the finger width and adjacent space of 300 μm was formed on the GO film. After the oxidative etching of uncovered GO caused by the oxygen plasma in the plasma cleaner, the patterned GO film was created. Finally, GO pattern was reduced to rGO pattern in hydrazine vapor. Before testing, Au film was sputtered on the square electrodes to enhance the conductivity of the electrodes. Structural analysis based on X-ray photoelectron spectroscopy (XPS) (Supplementary Figure S1) revealed the surface chemical properties of GO and rGO. Figure S1(a) and (b) exhibits the characteristic peaks of C 1S and O 1S in both samples respectively. Obviously, the O 1S peak intensity has increased from 7/3 in GO to 4/1 in rGO. The C 1S spectrum of the GO can be deconvoluted to three components corresponding to three types of carbon bonds within GO. The peaks centered at 284.6 eV, 286.8 eV and 286.3 eV, corresponding to C-C in aromatic rings, C-O in epoxy group and alkoxy group. The C 1S spectrum of rGO also shows three components with different proportions. The proportion of C-C bond (284.6 eV) has increased a lot for rGO. The C-O peak at 286.7 eV in epoxy group and alkoxy group has decreased, while some C-NH₂ bond at 285.3 eV aroused after hydrazine reduction. According the above results, a small portion of the C-O bonds were replaced by C-NH₂ and a large portion of the C-O bonds were reduced, indicating the successful formation of rGO [11].

In Figure 2(a), we display a digital photo of the obtained mSC device. In order to measure the thickness of the rGO film, we took the three dimensional view of the interdigital by a laser scanning confocal microscope. Figure 2(b) shows the planar optical images of the border between one of the rGO interdigital and the PET substrate. In this area, the relative height of rGO and PET was measured by laser scanning. As shown in Figure 2(c) and (d), PET represented
by green presents uniform lower height and the surface of rGO film presented by brown also exhibits uniform higher height except for several little bulges. The average height difference between the PET and the rGO was measured to be $1.2 \, \mu m$, according to the results of three measuring lines in the top, middle and bottom areas respectively. Credibly, the height difference on the right side was also turned out to be $1.2 \, \mu m$ (Figure 2(e) and (f)). Even though we observed several impurities on PET which may be missed by oxygen etching, interdigital was not short-circuited, demonstrating the feasibility of the mSC fabrication by a facile oxygen etching method.

The electrochemical characterization of the mSC was performed by two-electrode cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements. Figure 3(a) displays the CV curves of the mSC at the scan rates from 10 mV/s to 500 mV/s. In the voltage window ranging from 0 to 0.8 V, the CV curves exhibit a quasi-rectangular shape at low scan rates, showing no redox reactions. According to the CV curves, the maximum areal and volume capacitance were calculated to be $896.77 \, \mu F/cm^2$ and $8.01 \, F/cm^3$ respectively (Figure S3(a)). Meanwhile, the GCD curves at different current densities ranging from 22.5 to 90 $\mu A/cm^2$ were recorded in Figure 3(b), and the calculated maximum areal capacitance and volume capacitance were $781.70 \, \mu F/cm^2$ and $6.98 \, F/cm^3$ respectively (Figure S2(b)).

Cycling performance was also conducted as one of the basic properties of mSC. In Figure 3(c), after charging and discharging at the current density of 45.0 $\mu A/cm^2$ for 1500 times, the capacitance maintained at 93.4%, demonstrated a good cycling performance. The stability of the mSC under bent condition is an important parameter. In our work, the device after cycling test was bended at an angle of 150° for 20, 40, 60, 80 and 100 times respectively. Each CV curve in Figure 3(d) matches well with the initial curve after cycling, verifying the good flexibility under
bending conditions. Figure 3(e) depicts the energy density and power density of the mSC, which delivers a volume energy density of 0.621 mW h/cm³ at the power density of 0.782 W/cm³. The data of traditional supercapacitor, as well as a commercial Lithium thin-film battery (4 V/500 μA h), a commercial A&T lithium ion battery (800 mA h, 17500) and an Al electrolytic capacitor (3 V/300 μF) are investigated for comparison [1d,2a,6c,12]. Obviously, the as-fabricated mSC delivers a higher energy density than that of the traditional supercapacitors, approaching to the lithium thin-film battery and still far behind of the lithium ion batteries. To drive a photodetector, the output voltage of the energy unit should be stable. We also measured the self-discharge properties of the mSC and the corresponding result was shown in Figure 3(f). It can be seen that, after being

Figure 3 (a) Cyclic voltammograms (CV) of the microsupercapacitor at the scanning rates range from 10 mV/s to 500 mV/s. (b) Galvanostatic charge-discharge curves at different current densities. (c) The cycling charge-discharge stability of the microsupercapacitor at the current density of 45 μA/cm². (d) The CV curves of the flexible microsupercapacitor at the scanning rate of 100 mV/s measured before the cycling stability test and the bending stability with 150° angle for different times afterwards. (e) Ragone plot shows the comparison of the microsupercapacitor (dark squares) and a lithium thin-film battery (4 V/500 μA h), an A&T lithium ion battery (750 mA h), and an Al electrolytic capacitor. (f) The self-discharge curve of the microsupercapacitor.
charged to 0.8 V, the mSC maintained at 0.32 V for more than 9000 s, demonstrated the possibility of integrating the mSC with a photodetector device.

In order to achieve a flexible integrated on-chip photodetecting system, single-crystalline CdS nanowires were selected as the photoresponsive materials, which were produced via a conventional chemical vapor deposition method. Figure 4(a) presents the SEM image of the as-synthesized CdS nanowires, which clearly have the diameter of 100 to 200 nm and length of hundreds of micrometers, possessing high aspect ratio. The X-ray diffraction pattern of CdS nanowires in Figure S3 can be easily indexed to pure CdS with a hexagonal structure (JCPDS No. 77-2306). The sharp diffraction peaks in each crystal facets demonstrates the good crystallinity, which is fundamental for an excellent photodetector device [9b]. To confirm their photoresponsive properties, the I-V curves of the CdS nanowires assembled film were measured in the illumination of white light (15.21 mW/cm²) and in the dark, respectively. Obviously, the current between source electrode and drain electrode was linearly dependent with the applied voltage, illustrating the ohmic contact between electrodes and CdS nanowires, as can be seen in Figure 4(b). A much higher photocurrent than that in the dark indicates the excellent photoresponse of the CdS nanowires.

To get the flexible integrated photodetecting system, we printed CdS nanowires on the electrodes of the mSC as shown in Figure 4(c). The current collector of mSC acts as one electrode of the CdS photodetector while the middle square electrode between the mSC acts as another electrode. Figure 4(d) exhibits a digital photo of the flexible integrated photodetector driven by a microsupercapacitor. (e) Photocurrent versus time plots of the device under illumination at a bias of 0.32 V supplied by an external power source and driven by the microsupercapacitor respectively.
system under measurement on a probe station. The time-
dependent photoresponse of the flexible photodetecting
system was measured by periodically turning the white light
on and off, as shown in Figure 4(e). From the curve measured
with an external bias of 0.3 V, we find that, driven by the mSC,
the integrated photodetector showed stable and substantial
response to light illumination with a current on/off ratio of
34.50. The photoresponse of the CdS device driven by a
conventional external energy storage unit was also shown in
Figure 4(f) for comparison. A similar current on/off ratio of
34.74 in the case of a conventional external energy storage
unit was obtained, indicating the feasibility and stability of
the use of mSC to substitute the conventional energy unit as
driven source for a photodetector. Besides, we also found that
the photoelectric response time and recover time are 0.83 s
and 2.90 s for the mSC driven photodetector, which is even
more sensitive than external power source driven one (0.91 s
and 2.90 s). From our results, we deduced that, compared
with the conventional external energy unit, the use of the
mSC not only ensures stable and comparable performance, but
also provide new features such as excellent flexibility, micro-
miniaturization, and highly compact integration of the full
systems, which are believed to be integratable to the update
microelectronic technology.

To achieve a higher output voltage for the photodetecting
system, tandem mSCs are configured in series as shown in
Figure 5(a). For this system, three rGO-based mSCs were
integrated with a CdS nanowires-based photodetector. The
electrochemical performance of the tandem mSCs was
first investigated. Figure S4(a) compares the CV curves of a single
mSC to that of the tandem mSCs with the voltage window of
2.4 V at the scan rate of 200 mV/s. The tandem mSCs provide a
two-fold voltage window and a much smaller average current
than the single mSC. After integral calculation, we found that
the CV area of both devices are nearly the same, corresponding
well with the tandem principle of supercapacitors: $1/C = \sum_{i=1}^{n} 1/C_i$. A series of CV scanning rates ranging from
20 mV/s to 5 V/s were conducted on the tandem mSCs, as

![Figure 5](image_url)

(a) The digital photograph of the as-fabricated tandem microsupercapacitor. (b) The self-discharge curve of the tandem
microsupercapacitor. (c) The schematic illustration of the electric circuit and (d) the photograph of the self-powered photodetector
driven by the tandem microsupercapacitor. (e) Photocurrent versus time plots of the device under illumination at a bias of 0.8 V
supplied by an external power source and driven by the tandem microsupercapacitor respectively.
shown in Figure S4(b) and (c). With the increase of scanning rate up to 5 V/s, the shape of the CV curves distorted little, demonstrating the fast charge-discharge ability and stability of the device. According to above CV results, the maximum capacitance of the tandem mSC was calculated to be 250 μF (Figure 5(a)). However, the gradually dropped capacitances at increased scanning rates indicate the inferior conductivity of the tandem rGO mSCs, which could be further optimized in the future. The GCD curves were also tested at the current of 33.3 and 66.6 μA (Figure S5(b)), delivering a capacitance of 117.6 and 101.9 μF respectively, showing a stable working condition. The self-discharge performance in Figure 5(b) discloses that the tandem mSCs could maintain at 0.8 V after being fully charged for more than 1700 s, indicating possible long time possibility to power electronic and photoelectronic devices.

The photoresponse properties of the CdS nanowire-based photodetector in the integrated photodetecting system were then studied. The schematic circuit illustration and the real testing system are exhibited in Figure 5(c) and (d) respectively. We compared the time-dependent photoresponse of the photodetector driven by an external power source with the integrated device (Figure 5(e)). With the illuminating light periodically on/off, the photocurrent was stimulated and recovered periodically. Current on/off ratios of 79.81 and 84.53 were obtained for the two systems, respectively, indicating obviously comparable performance of the mSCs integrated system with that of the external power source driven system. The photoelectric response time and recover time are 0.83 s and 2.90 s for the self-powered photodetector, corresponding well with that of the external power source driven one (0.73 s and 2.90 s). Therefore, we further demonstrated the feasibility and stability of the flexible integrated photodetecting system with mSCs as the driven source.

Conclusions

In this work, we demonstrated a prototype of a fully flexible photodetecting system by integrating a rGO-based in-plane microsupercapacitor with a CdS nanowire-based photodetector. The device was fabricated by micropatterning of GO film on flexible substrates, which is simple, reliable and can be scaled up for large scale integration circuit. The optimized electrodes in the microsupercapacitor device were utilized as the source and drain electrodes of the CdS photodetector as well, configuring a self-powered-like visible light photodetector without external power source. Current on/off ratios of 34.50 and 79.81 were obtained by the individual and tandem microdevices respectively, exhibiting a photo-current response consistent with the one driven by the external power source. Further improvement of the graphene films, such as film thickness and conductivity, development of new film manufacturing and reducing process, modification of the configuration would definitely enhance the performance of the microsystem.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2015.02.027.

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