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Photo-responsive Properties on Locally Confined Ultrathin Silicon Nanowires

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Abstract: Functional ultrathin silicon nanowires (SiNWs) are promising building blocks for high responsive photo-detectors and ultra-high sensitive bio-chemical sensors. In this work we investigate the photo responsive characteristics of of ultrathin SiNW arrays fabricated using a novel top-down process. The fabricated SiNW arrays were able to detect light from the UV to the visible range with good sensitivity and ultrahigh photo-responsivity ($R \sim 10^4$ A/W). In addition, the SiNWs displayed good stability and reliability over long-term measurements at different temperatures (273 – 343 K) in both forward and reverse bias directions. By sensitizing the fabricated SiNW arrays with cadmium telluride (CdTe) quantum dots (QDs), hybrid QD SiNW arrays were created and displayed a significant improvement in photocurrent response under UV light, while preserving their performance in the visible light range. The fast, stable and high photo response of these new hybrid nanostructures is very promising towards the development of novel optoelectronic and photovoltaic devices.

Keywords: Ultrathin silicon nanowires; locally-thinned down; top-down fabrication; photo responsive; quantum dot.

1. Introduction

Silicon nanowires (SiNWs) are an exciting class of nanomaterials and their unique properties have been already demonstrated in a range of technological applications [1-4]. This is due to their remarkable physical properties, such as their high performance field-effect transistors (FET) [5, 6] and ultrahigh photo-responsivity [7]. SiNWs are therefore actively being integrated in hybrid nanoscale devices for applications in biosensing [8], optoelectronics [4, 9, 10] and photovoltaics [2, 11-13]. Owing to quantum confinement effects and their promising electrical performances (e.g. high carrier mobility, high drive current, near ideal sub-threshold slop and high current on/off ratio), ultralow dimensional SiNWs (sub-20 nm cross-section) is promising for further advances in nanoelectronics [14-17]. Contrary to conventional silicon photo detector, which has limited photo detection capabilities in the visible and near infrared light range, photo detectors based on SiNW structures are able to detect ultraviolet light with high responsivity [7, 18]. This unique property makes SiNWs promising building blocks for high performance photo-detectors and full-spectrum photovoltaic devices. Although SiNWs have been known for their excellent light trapping efficiency, device performance may be limited due to light reflection. This is especially common on planar SiNWs where the low fill factor would significantly reduce net detection efficiency and hence reduce the SiNWs device performance.

Herein, we present a concept of ultrathin SiNW arrays fabricated by a novel top-down process that is able to detect light from the UV to the visible range with good sensitivity (limit of detection ~ 0.75 mW.cm⁻²), fast response and high photo-responsivity ($R = 10^4$ A/W). In addition, the fabricated SiNWs devices have successfully demonstrated stability and reliability over long-term measurements in a range of different temperatures (0°C – 70°C) in both forward and reverse bias directions. Furthermore, by sensitizing the SiNWs with cadmium telluride (CdTe) quantum dots (QDs), the hybrid device has shown an average of ~ 59 % of improvement in photocurrent response in comparison with the control samples under UV light while preserving performance in visible light. The fast, stable and high photo response of the new hybrid nanostructures is very promising towards the development of novel optoelectronic and photovoltaic devices.

2. Results and Discussion

The ultrathin SiNWs has been fabricated at the wafer-scale and packaged in a chip unit (length – 17 mm, width - 8 mm) with 4 independent nanowire arrays (8 nanowires/array) and connected to separate source/drain electrodes (S/D) as shown in Figure 1. Using our optimized tetramethylammonium hydroxide (TMAH) wet-etching process [17], we were able to locally thin down the nanowire to sub-20 nm without impacting on the remaining structures, hence not compromising the electrical contacts. As seen in the SEM images presented in Figure 1, the prepared SiNW arrays could be reliably thinned down to 20 nm in their middle regions.

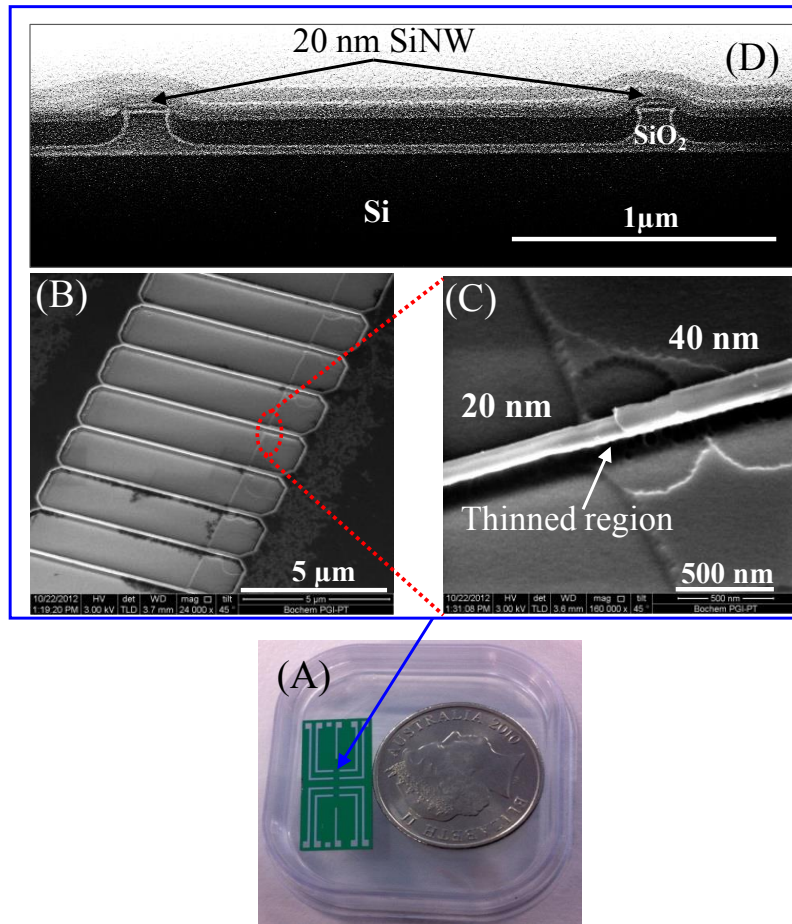


Figure 1. SiNWs on-a-chip unit (A), SEM images of locally confined ultrathin SiNW arrays fabricated on silicon on-insulator wafer (SOI) (B). High magnification SEM of a single ultrathin SiNW with 20 nm thinned region (C). (D) FIB cross-sectional images at the thinned regions of the 20 nm SiNWs.

The fabricated ultrathin SiNWs with 20nm thicknesses were characterized at room temperature using a custom-built 16-channel low-noise amplifier system equipped with a dark chamber modified from [19]. First, the opto-electrical response of the device was measured using monochromatic red light irradiation (peak wavelength at ~ 680 nm) generated by a light-emitting diode (LED) light source. When increasing the light intensities from 0 to 0.5 – 1.5 – 4.5 – 12.5 $\text{mW}\cdot\text{cm}^{-2}$, the device clearly showed an increased photocurrent response in the forward ($V_{\text{ds}} = 0 \rightarrow 3.0$ V) and reverse bias ($V_{\text{ds}} = 0 \rightarrow -3.0$ V) directions with respect to the dark conditions (Figure 2A). It is well-known that the photosensitive nature of the silicon photo-detector relies on the photo-generation and instant separation of electron-hole pairs under electrical fields [7, 12]. When light reaches the SiNWs, the photon energy can be absorbed and generate electron-hole pairs in the nanowires. The absorption depth of photons in silicon is dependent on the photon energy. The shorter the wavelength (higher photon energy), the shallower the absorption. When generated in such ultrathin SiNWs, the electron-hole pairs are separated immediately by the electric field [4, 11]. The electrons recombine with trapped holes at the interface between Si/SiO₂ while the photo-generated holes remains in the core of the nanowires and

contribute to the increasing of the output current. As the light intensity increases, more electron-hole pairs are created and lead to increasing of the photocurrent.

In comparison with recent reports [7, 20], the photocurrents demonstrated in our device were observed to be symmetrically dependent on the light intensities using both forward and reverse bias voltages. We hypothesize that this originates from the overall structure of the ultrathin SiNW arrays resulting from the one-step selective size reduction. The process preserves the continuous connection of the silicon layer from the ultrathin nanostructures to the micro contact areas and hence facilitates efficient and symmetrical electrical interconnection between nanowires and metal electrodes. From the dynamic time response of the device, the minimum detectable light intensity has been demonstrated to be approximately 0.75 mW.cm^{-2} . This is remarkable considering the very limited sensing areas on the device (c.a. $12 \text{ }\mu\text{m}^2/\text{array}$) (Figure 2B). The photo-responsivity at 10 mW.cm^{-2} of light irradiation under 3.2 V biased voltage has been calculated at $R \sim 5.10^4 \text{ A/W}$, which is several orders of magnitude higher than the current benchmarks of conventional silicon PIN photodiodes (0.7 A/W) and avalanche photodiode (140 A/W). At 3.2 V biased voltage, the time-response of the ultrathin SiNWs has been measured to be approximately 3.0 ms (Figure 2C). We expect that the time-response could be faster if measured with a set-up with higher sampling rate than that of our current instrument (1000 data points/s).

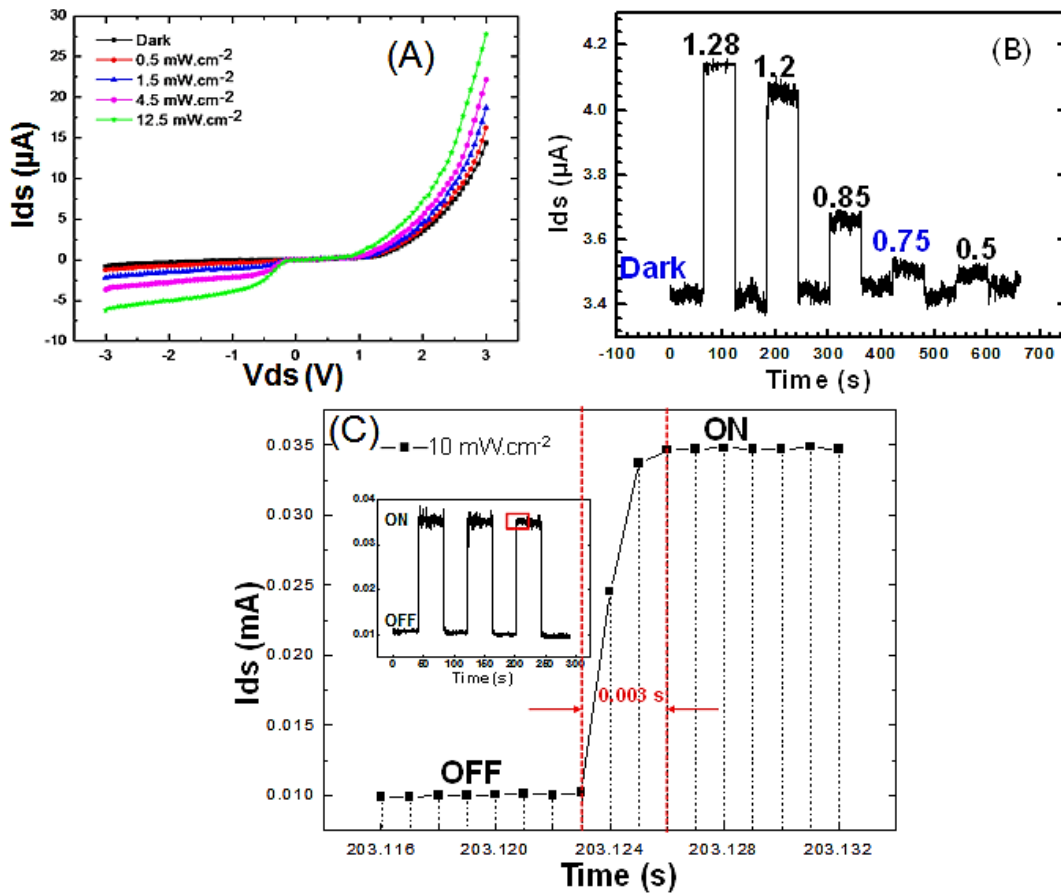


Figure 2. Photo responses of as-fabricated ultrathin SiNWs measured under different red light intensities (A). Dynamic current-time curves with periodical light on/off conditions; light intensities are at $1.28 - 1.2 - 0.85 - 0.75 - 0.5 \text{ mW.cm}^{-2}$, V_{ds} is at 2.14 V (B). Photocurrent time- response

curves of SiNWs under 10 mW.cm^{-2} of light intensity (ON) and in the dark (OFF) with bias voltage at 3.2 V. The time response curve has been magnified from the dynamic time response of the nanowire device at the inset plot (red square).

The temperature photocurrent dependence and its long term stability have been demonstrated in Figure 3 A and 3B, respectively. As seen in figure 3A, no detectable photocurrent signal degradation was observed at 5 mW.cm^{-2} of light intensity for temperatures ranging from 273 to 343K. Poor thermal stability is the main limitation of nanoscaled photo-detectors [21, 22], however the fabricated devices maintained their high performance even well above room temperature. Next, the reliability of the SiNWs was demonstrated through long term measurements of the photocurrent response (Fig 3B). The stability was observed in both forward and reversed bias voltages for 15 minutes of continuous measurements at 1.5 mW.cm^{-2} light intensity. The optical response of the SiNWs was characterized under dark conditions as well as different monochromatic light wavelengths ranging from UV to the visible (254 – 680 nm). The photocurrents increased with the different light wavelengths. However, the device showed lower stability in the UV-wavelength at 254 and 365 nm due to the inherent fluctuation of the UV light intensity of the Hg lamp (Figure 3C).

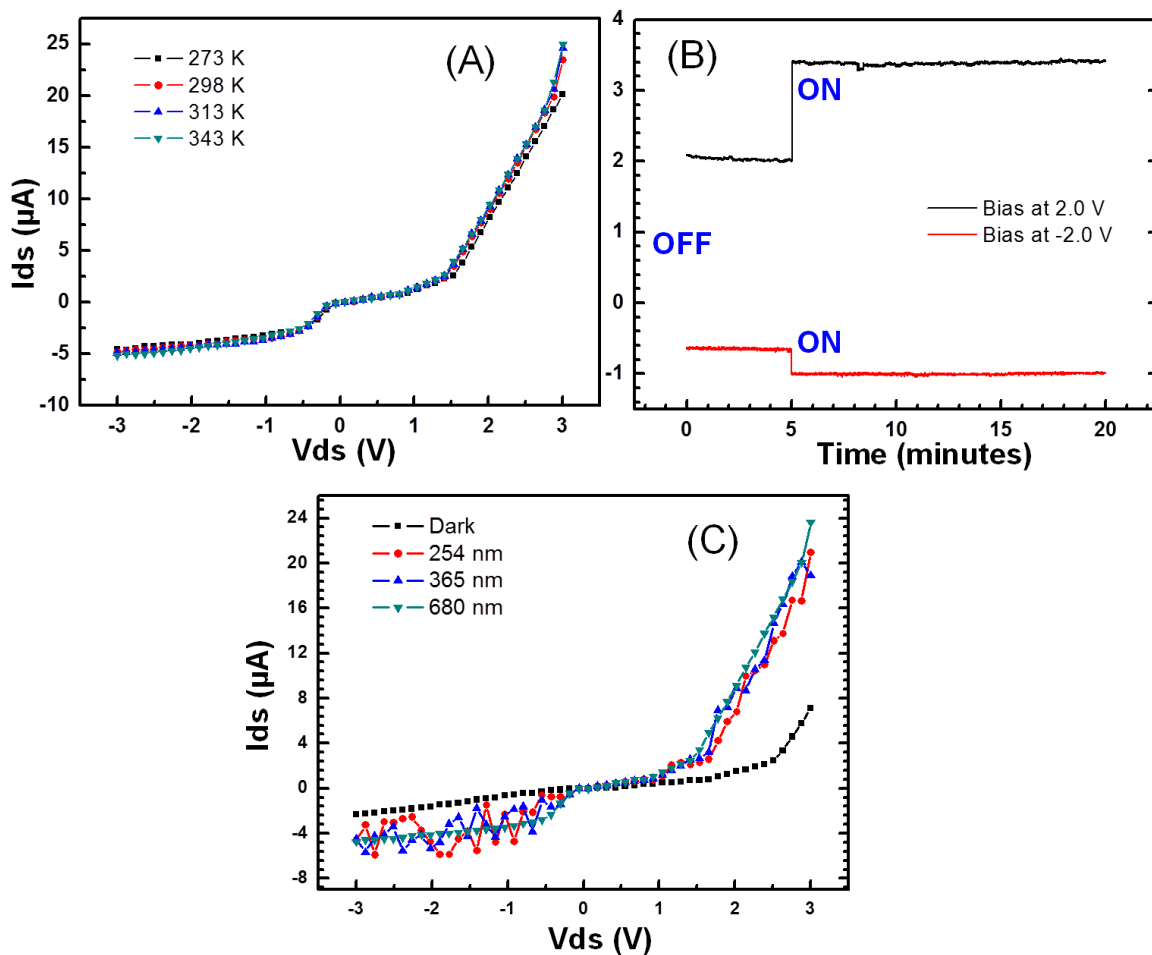


Figure 3. Photo-current dependence of as-fabricated SiNWs on different measuring temperatures at 5 mW.cm^{-2} (A) and the photo-current response of the fabricated SiNWs over 15 minutes of 1.5 mW.cm^{-2} red light irradiation at 2.0 V and -2.0 V biased voltages (B). I-V characteristic of the SiNWs

in different monochromatic light wavelength from 254, 365 and 680 nm, light intensity at $5 \text{ mW}\cdot\text{cm}^{-2}$ (C).

To further increase the sensitivity of the SiNW device, a novel approach was investigated based on the sensitization with QDs. A thin coating of QD with an emission peak at 550 nm (Supplementary information) was formed on the SiNWs and the photoresponse of the hybrid device was investigated at various wavelengths. As shown in Fig.4, UV light irradiation of the Si-QD structures resulted in increased photocurrent in comparison to SiNWs without QDs sensitization. The increase in photocurrent response was approximately $59 \pm 10 \%$ in the linear regions of the photo current (i.e. photocurrent regions at $V_{ds} > 2.5 \text{ V}$) when compared with the control bare SiNWs measured at a wavelength of 365 nm. On the other hand, no difference was observed between the sensitized and non-sensitized SiNWs under visible light (680 nm). We hypothesize here that under UV irradiation at 365 nm, the CdTe QDs used here are excited and emit visible light at $\sim 500 \text{ nm}$, contributing to the increase in photocurrent as seen in Figure 4. Importantly, the presence of the QDs does not compromise the performance in the visible range. Initial measurement of QD sensitized ultrathin SiNWs in solar full-spectrum (wavelength: $300 \rightarrow 1400 \text{ nm}$; $100 \text{ mW}/\text{cm}^2$) showed an increased photocurrent when compared to the untreated SiNW devices (Supplementary information). However, the photocurrent change was not significant which might be due to the very low number of photoactive SiNWs used in this study (8 nanowires/channel) and the relatively low ratio of UV light in the solar full-spectrum (c.a. 10%). By further optimizing the number of nanowires per unit chip, we expect that QD sensitized ultrathin SiNW arrays will open promising applications in optoelectronic switches, photo detectors and hybrid photovoltaic devices.

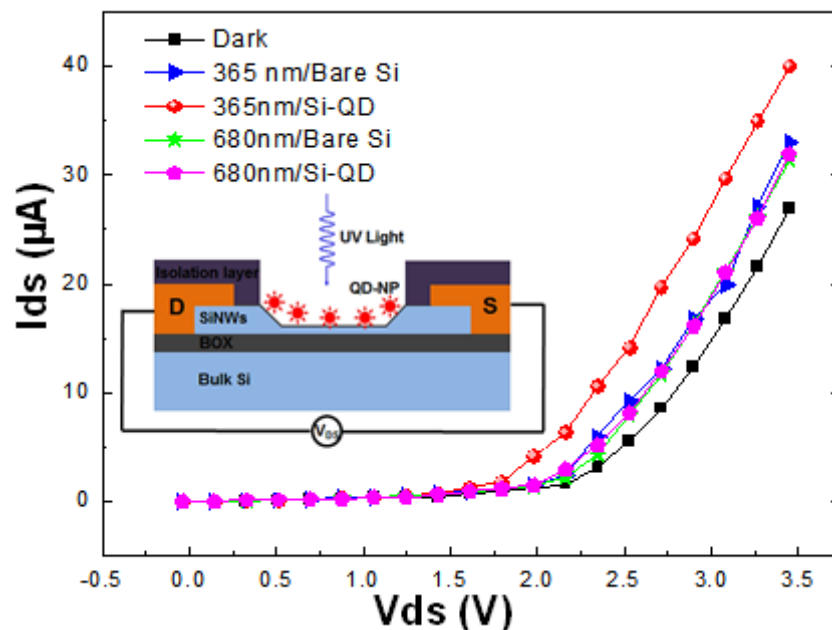


Figure 4. Photo response of bare ultrathin SiNWs and CdTe QD sensitized SiNWs under UV (365 nm wavelength) light irradiation and response of control device, measured in red light (680 nm

wavelength). The dark current is measured with bare SiNWs. Inset shows the schematic for SiNW QD hybrid device. Light intensities are at 5 mW.cm^{-2}

3. Experimental Section

The novel top down wafer-scale fabrication process to prepare locally confined ultrathin SiNWs has been described in details previously [17]. Briefly, a thin ($44 \pm 2 \text{ nm}$) homogenous dry-oxidized silicon dioxide (SiO_2) layer was formed on top of p-type SOI wafer (SOITEC; B: $1 \times 10^{15} / \text{cm}^3$; BOX: 145 nm ; Si device layer: 70 nm) to serve as a mask for the initial TMAH etching step. Wafer-scale aluminum (Al) nanostructures were then patterned on the dry-oxidized SiO_2 by means of e-beam writing on PMMA photoresist and subsequent Al lift-off process. The Al patterns were used as a metal mask to transfer their structures on the SiO_2 layer beneath using reactive ion-etching. Next, the entire Al pattern was removed using an Al etchant AZ MIF 326 followed by the first TMAH wet-etching step (25wt %; 80°C with agitation). Another dry-oxidized SiO_2 layer ($\sim 15 \text{ nm}$ in thickness) was again formed on the wafer followed by a conventional photolithography step to open windows in the middle section of the nanowires. In the next step, the wafer was step-etched using an optimized TMAH wet-etching process for 40 seconds (25wt% TMAH with 10vol% IPA, 35°C , agitation). This anisotropic step-etching thinned down the unprotected silicon nanowires in the middle sections of the nanowires to about 20 nm and 15 nm in the (100) direction while the rest of the nanostructures retained their original thicknesses due to the silicon dioxide mask. Finally, the wafer was selectively ion-implanted (B; $1 \times 10^{15} / \text{cm}^2$) at the contact regions followed by an Al lift-off step to form metal feed lines for the fabricated nanowires. A thick hard-baked AZ1518 photoresist ($\sim 1.5 \mu\text{m}$) was employed as a passivation layer on the contacts. The wafer was finally diced in small chips with a typical size of $18 \times 8 \text{ mm}$ and packaged in a ready-to-test ceramic chip socket. A layer of dark epoxy glue has been employed as a light blocking layer to protect the metal parts during the optical characterizations. The opto-electrical response of the device was measured under ultraviolet light (wavelength at 254 nm and 365 nm) and monochromatic red light (wavelength at 680 nm) irradiation generated by a low pressure mercury lamp and a light-emitting diode lamp, respectively.

Synthesis of CdTe QD. A modified literature method was used for the synthesis of NaHTe [23]. First, 37.8 mg (1mM) of dry NaBH_4 was loaded into a 25 mL flask under an inert atmosphere. 50.8 mg (0.4 mM) of tellurium powder and 10.0 mL of distilled water was then added. The flask was pumped with Ar for 10 minutes to ensure the atmosphere was inert. Under Ar, the solution was mixed at 90°C for 45 minutes or until the solution turned a clear purple colour. The solution was stored under Ar at room temperature until required. CdTe QDs were then synthesized in the aqueous phase. Briefly, 36.66 mg (0.2 mmol) of CdCl_2 and 30 μL (0.34 mmol) of MPA was added to 40 mL of DI water. The pH was then adjusted to 12 using 1.0 M NaOH. Upon addition of the NaOH the solution goes cloudy before returning to clear once the desired pH has been reached. NaHTe was injected at room temperature and heated to 100°C . CdTe QDs were then grown over the period of 1-2 hrs, and the colour of the solution changed from yellow to orange as time progressed. CdTe QDs with an emission peak at 500 nm were used in this study.

4. Conclusions

The photo-responsive properties on ultrathin SiNWs have been studied. By using an advanced SiNWs novel top-down fabrication process, we were able to efficiently detect light from the UV to the visible range and achieve good stability, reliability and photo-responsivity. Furthermore, by sensitizing the SiNWs with CdTe QDs, an improvement in the photocurrent response under UV illumination of 59% was obtained, while preserving their performance in the visible light. This novel approach is therefore promising for the development of novel hybrid photo-responsive nanostructures in the areas of photovoltaics and optoelectronics.

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Conflicts of Interest

The authors declare no conflict of interest

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Supplementary information

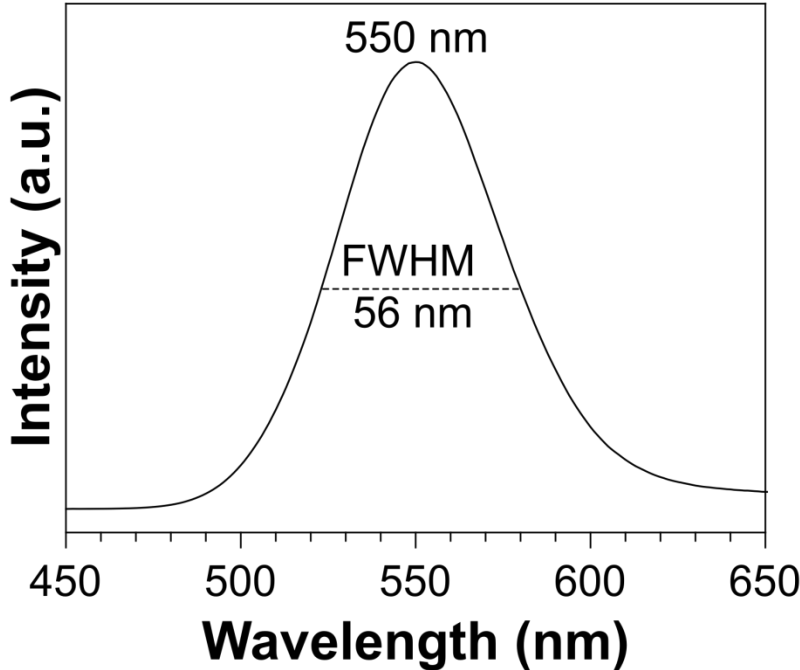


Fig.1. Emission spectra of the synthesized CdTe quantum dot nanoparticles.

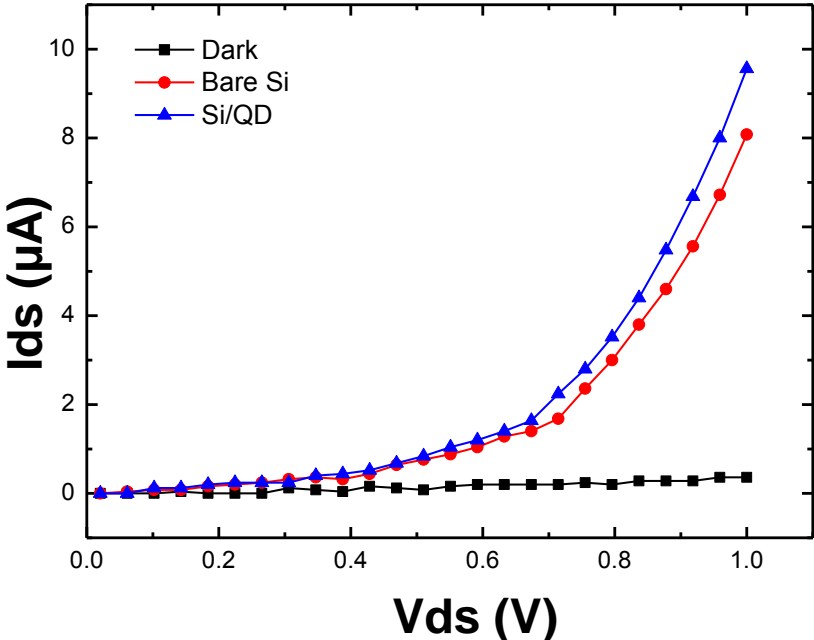


Fig.2. Photo-responses of the bare SiNWs device and QD-SiNWs device measured under the solar full-spectrum (wavelength: 300 → 1400 nm; 100 mW/cm²). The dark current was monitored on the bare SiNWs device.