

**NANO EXPRESS**

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# Photoconductivities in monocrystalline layered $V_2O_5$ nanowires grown by physical vapor deposition

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## Abstract

Photoconductivities of monocrystalline vanadium pentoxide ( $V_2O_5$ ) nanowires (NWs) with layered orthorhombic structure grown by physical vapor deposition (PVD) have been investigated from the points of view of device and material. Optimal responsivity and gain for single-NW photodetector are at  $7,900 \text{ A W}^{-1}$  and 30,000, respectively. Intrinsic photoconduction (PC) efficiency (i.e., normalized gain) of the PVD-grown  $V_2O_5$  NWs is two orders of magnitude higher than that of the  $V_2O_5$  counterpart prepared by hydrothermal approach. In addition, bulk and surface-controlled PC mechanisms have been observed respectively by above- and below-bandgap excitations. The coexistence of hole trapping and oxygen sensitization effects in this layered  $V_2O_5$  nanostructure is proposed, which is different from conventional metal oxide systems, such as ZnO,  $\text{SnO}_2$ ,  $\text{TiO}_2$ , and  $\text{WO}_3$ .

**Keywords:** Vanadium pentoxide; Nanowire; Photoconductivity; Physical vapor deposition; Normalized gain

## Background

Vanadium pentoxide ( $V_2O_5$ ) is the most stable crystallization form and is also the most applicable in the industry among vanadium oxide systems such as VO,  $\text{VO}_2$ , and  $\text{V}_2\text{O}_3$ . The orthorhombic layered structure of  $V_2O_5$  promises a high ionic storage capacity for energy storage applications [1]. Recently, its quasi-one-dimensional nanostructures such as nanowires (NWs), nanobelts (NBs), and nanotubes have gained substantial attention. Due to high surface-to-volume ratio and high surface activity,  $V_2O_5$  1D structures for various applications, such as field emitters [2-5], transistors [6,7], chemical sensors [8-10], and lithium batteries [11-14], have been developed.

In addition,  $V_2O_5$  with a direct optical bandgap at visible-light region ( $E_g = 2.2$  to  $2.7 \text{ eV}$ ) [2,15-18] also inspires the studies of optoelectronic applications such as photodetection [2,19], optical waveguide [20], and high-speed photoelectric switch [21]. Although device performance of the individual NW has been demonstrated in several studies, fundamental photoconduction (PC)

properties and their corresponding surface effects were less studied than the known hopping transport [6,21-24]. The potential difference of the transport properties of nanomaterials grown by different approaches was also less known. In this paper, we report the study of photoconductivities of  $V_2O_5$  NWs grown by physical vapor deposition (PVD). The performance of the single-NW device and intrinsic PC efficiency of the material have been defined and discussed. The results are also compared with the reported data of the  $V_2O_5$  counterpart synthesized by hydrothermal approach. The probable PC mechanisms that originated from the bulk and surface under above- and below-bandgap excitations are also proposed.

## Methods

$V_2O_5$  NWs were grown by PVD using high-purity  $V_2O_5$  powder as the source material and mixed  $\text{O}_2/\text{Ar}$  as the carrier gas. The growth temperature was  $550^\circ\text{C}$ , and the pressure was 0.3 Torr. The details of material growth can be found in our earlier publications [25,26]. The morphology, structure, and crystalline quality of the as-grown  $V_2O_5$  NWs were characterized by field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), Raman spectroscopy, high-resolution transmission electron microscopy (HRTEM), and selected-area electron

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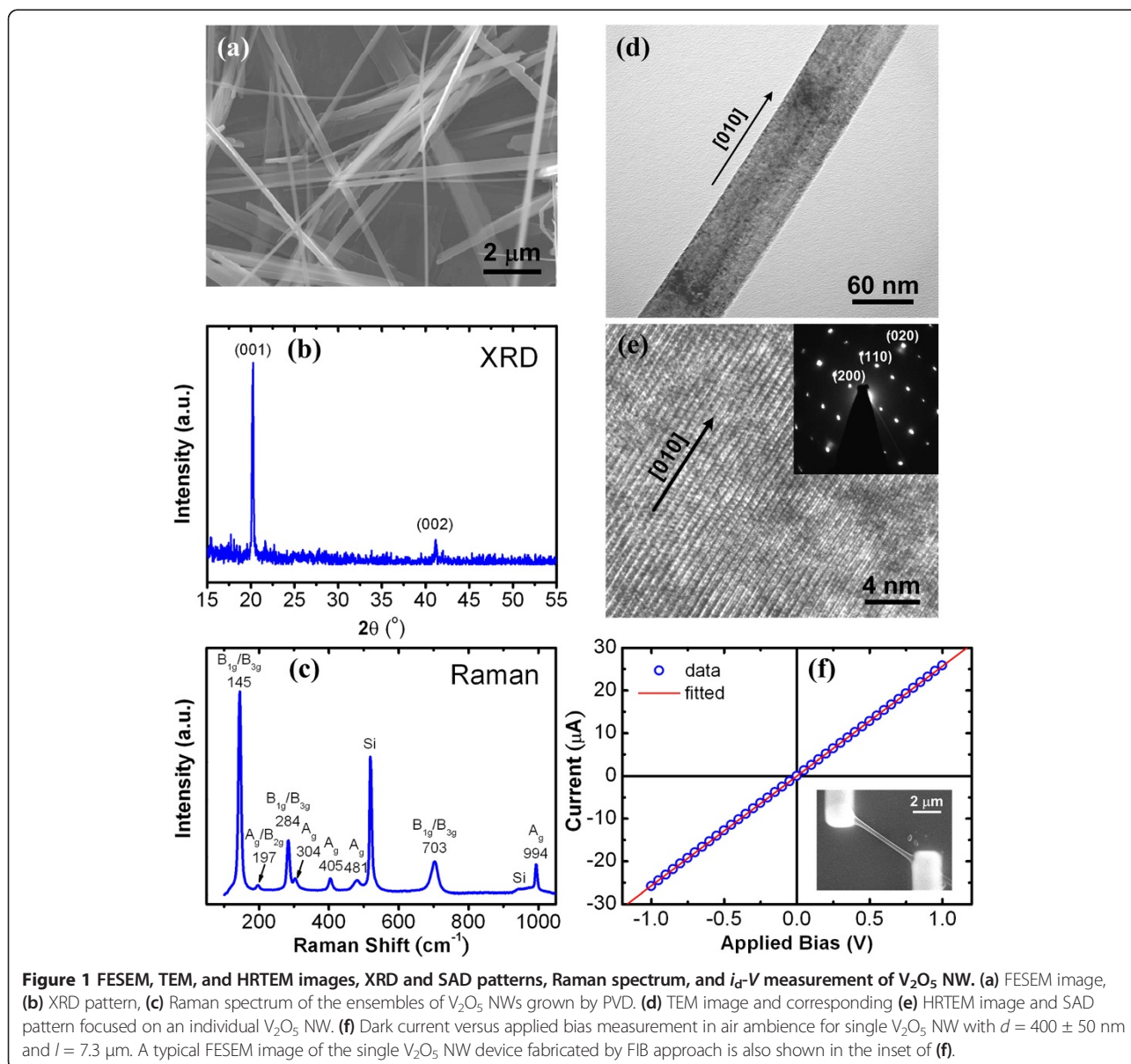
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diffraction (SAD). Electrical contacts of the two-terminal single-NW devices were fabricated by focused ion beam (FIB; FEI Quanta 3D FEG, FEI Company, Hillsboro, OR, USA) deposition using platinum (Pt) as the metal electrode. Individual NWs were dispersed on the insulating  $\text{Si}_3\text{N}_4/n\text{-Si}$  or  $\text{SiO}_2/n\text{-Si}$  template with pre-patterned Ti/Au microelectrodes prior to FIB deposition. Electrical measurements were carried out on an ultralow-current leakage cryogenic probe station (TTP4, LakeShore Cryotronics, Inc., Westerville, OH, USA). A semiconductor characterization system (4200-SCS, Keithley Instruments Inc., Cleveland, OH, USA) was utilized to source dc bias and measure current. He-Cd gas laser and diode laser were used to source excitation lights with wavelengths ( $\lambda$ ) at 325 and 808 nm for the PC measurements, respectively.

The incident power of laser was measured by a calibrated power meter (Ophir Nova II, Ophir Optronics, Jerusalem, Israel) with a silicon photodiode head (Ophir PD300-UV). A UV holographic diffuser was used to broaden laser beam size (approximately  $20 \text{ mm}^2$ ) to minimize error in power density calculation.

## Results and discussion

A typical FESEM image of  $\text{V}_2\text{O}_5$  NW ensembles grown as described above on silicon substrate prepared by PVD is shown in Figure 1a. The micrograph reveals partial  $\text{V}_2\text{O}_5$  1D nanostructures with slab-like morphology. The diameter ( $d$ ), which is defined as the width of the NWs with relatively symmetric cross section, is in the range of 100 to 800 nm. The length usually is longer than  $10 \mu\text{m}$ . The

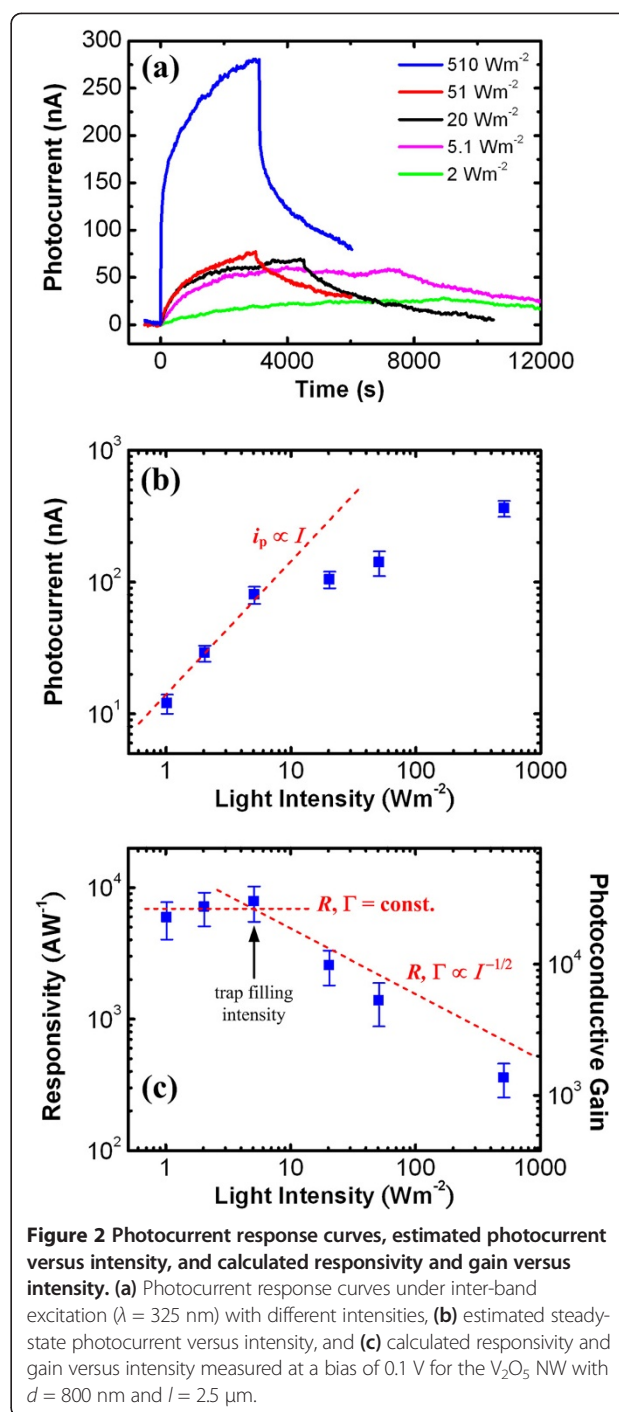


**Figure 1** FESEM, TEM, and HRTEM images, XRD and SAD patterns, Raman spectrum, and  $i_d$ - $V$  measurement of  $\text{V}_2\text{O}_5$  NW. (a) FESEM image, (b) XRD pattern, (c) Raman spectrum of the ensembles of  $\text{V}_2\text{O}_5$  NWs grown by PVD. (d) TEM image and corresponding (e) HRTEM image and SAD pattern focused on an individual  $\text{V}_2\text{O}_5$  NW. (f) Dark current versus applied bias measurement in air ambience for single  $\text{V}_2\text{O}_5$  NW with  $d = 400 \pm 50 \text{ nm}$  and  $l = 7.3 \mu\text{m}$ . A typical FESEM image of the single  $\text{V}_2\text{O}_5$  NW device fabricated by FIB approach is also shown in the inset of (f).

XRD pattern shows the predominant diffraction peaks at 20.3° and 41.2° (Figure 1b), which is consistent with the (001) and (002) orientations of the orthorhombic structure (JCPDS no. 41-1426). The Raman spectrum shows the eight signals at positions of 145 cm<sup>-1</sup> (B<sub>1g</sub>/B<sub>3g</sub>), 197 cm<sup>-1</sup> (A<sub>g</sub>/B<sub>2g</sub>), 284 cm<sup>-1</sup> (B<sub>1g</sub>/B<sub>3g</sub>), 304 cm<sup>-1</sup> (A<sub>g</sub>), 405 cm<sup>-1</sup> (A<sub>g</sub>), 481 cm<sup>-1</sup> (A<sub>g</sub>), 703 cm<sup>-1</sup> (B<sub>1g</sub>/B<sub>3g</sub>), and 994 cm<sup>-1</sup> (A<sub>g</sub>), which correspond to the phonon modes in previous reports [17,27,28], further confirming the orthorhombic crystalline structure of the V<sub>2</sub>O<sub>5</sub> NWs (Figure 1c). Two major Raman peaks at low-frequency positions of 145 and 197 cm<sup>-1</sup> that originated from the banding mode of (V<sub>2</sub>O<sub>2</sub>)<sub>n</sub> also indicate the long-range order layered structure of V<sub>2</sub>O<sub>5</sub> NWs. In addition, the single-crystalline quality of the V<sub>2</sub>O<sub>5</sub> NWs is further confirmed by the TEM and SAD measurements. Figure 1d shows the TEM image focused on an individual V<sub>2</sub>O<sub>5</sub> NW. The clear lattice image can be observed by HRTEM as depicted in Figure 1e. The preferential growth orientation of long axis along <010> is also confirmed by the corresponding SAD pattern with zone axis along <001> as shown in the inset of Figure 1e [12].

Electrical contacts of single V<sub>2</sub>O<sub>5</sub> NW devices were examined by dark current versus applied bias (*i<sub>d</sub>*-*V*) measurements. Figure 1f depicts typical *i<sub>d</sub>*-*V* curves measured at room temperature of 300 K for the V<sub>2</sub>O<sub>5</sub> NW with *d* at 400 ± 50 nm and the inter-distance between two contact electrodes (*l*) at 7.3 μm. A representative FESEM image of the individual V<sub>2</sub>O<sub>5</sub> NW device is also shown in the inset of Figure 1f. The *i<sub>d</sub>*-*V* curve reveals a linear relationship, indicating the ohmic contact condition of the NW device. Room temperature conductivity ( $\sigma$ ) was estimated at 13 ± 3 Ω<sup>-1</sup> cm<sup>-1</sup>. A similar  $\sigma$  can be reproduced from the other samples with a *d* range of 200 to 800 nm. The  $\sigma$  level is more than one order of magnitude higher than that ( $\sigma = 0.15$  to 0.5 Ω<sup>-1</sup> cm<sup>-1</sup>) of individual V<sub>2</sub>O<sub>5</sub> NWs in previous reports in which small polaron hopping is attributed to the transport mechanism [23,24].

The photocurrent response curves for the 325-nm band-to-band excitation under different light intensity (*I*) at a bias of 0.1 V for the V<sub>2</sub>O<sub>5</sub> NW with *d* = 800 nm and *l* = 2.5 μm are illustrated in Figure 2a. A constant background current has been subtracted to reveal the photocurrent values. The result shows that the photo-response takes a rather long time to reach a steady state. The estimated steady-state photocurrent (*i<sub>p</sub>*) versus *I* is plotted in Figure 2b. The *i<sub>p</sub>* shows a linear increase with the increase of *I* below a critical power density at approximately 5 W m<sup>-2</sup>. Once *I* exceeds the critical value, the *i<sub>p</sub>* deviates from the linear behavior and appears to saturate gradually. To investigate the device performance and PC mechanism underneath the power-dependent *i<sub>p</sub>*, two quantities, namely responsivity (*R*) and photoconductive gain ( $\Gamma$ ) which determine the photodetector performance, will be defined and discussed.



**Figure 2** Photocurrent response curves, estimated photocurrent versus intensity, and calculated responsivity and gain versus intensity. (a) Photocurrent response curves under inter-band excitation ( $\lambda = 325$  nm) with different intensities, (b) estimated steady-state photocurrent versus intensity, and (c) calculated responsivity and gain versus intensity measured at a bias of 0.1 V for the V<sub>2</sub>O<sub>5</sub> NW with *d* = 800 nm and *l* = 2.5 μm.

The responsivity *R* is defined as the photocurrent generated by the power of light incident on an effective area of photoconductor, i.e.,

$$R = \frac{i_p}{P_{NW}}$$

where *P<sub>NW</sub>* is the incident optical power on the projected area (*A*) of the measured NW and can be

calculated as  $P_{NW} = IA = Idl$  [29]. The calculated  $R$  versus  $I$  result according to the measured  $i_p$  values in Figure 2b is depicted in Figure 2c. The result shows that  $R$  increases from 360 to 7,900  $A W^{-1}$  gradually and saturates at a near-constant level while intensity decreases from 510 to 1  $W m^{-2}$ . While comparing the optimal  $R$  with that of earlier reports, the value at 7,900  $A W^{-1}$  is over one order of magnitude higher than that ( $R \sim 482 A W^{-1}$ ) of  $V_2O_5$  NWs synthesized by hydrothermal approach [2]. Even if the comparison is made at similar power densities in the range 20 to 30  $W m^{-2}$ , the PVD-grown  $V_2O_5$  NW still exhibits higher  $R$  at approximately 2,600 than the reference data by a factor of 5. In addition, compared to other nanostructured semiconductor photodetectors, the  $R$  of the  $V_2O_5$  NW device is higher than those of ZnS NBs ( $R \sim 0.12 A W^{-1}$ ) [30], ZnSe NBs ( $R \sim 0.12 A W^{-1}$ ) [31], ZnO nanospheres ( $R \sim 14 A W^{-1}$ ) [32], and  $Nb_2O_5$  NBs ( $R \sim 15 A W^{-1}$ ) [33] and is lower than those of GaN NWs ( $R \sim 10^6 A W^{-1}$ ) [34] and ZnS/ZnO biaxial NBs ( $R = 5 \times 10^5 A W^{-1}$ ) [35].

To investigate the  $\Gamma$  which is a physical quantity determining the photocarrier collection efficiency of a photodetector,  $\Gamma$  is estimated according to its linear relationship with  $R$  and  $i_p$ , i.e.,

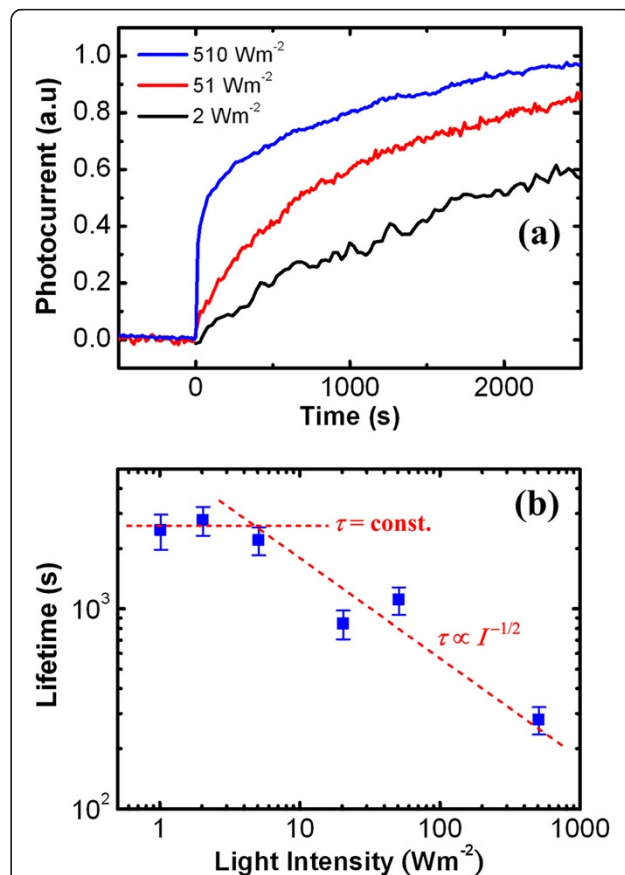
$$\Gamma = \frac{E}{e} \frac{R}{\eta} = \frac{E}{e} \frac{i_p}{\eta P},$$

where  $E$  is the photon energy,  $e$  is the elementary electron charge, and  $\eta$  is the quantum efficiency [29]. To simplify the calculation, the  $\eta$  is assumed to be unity. The calculated  $\Gamma$  versus  $I$  result is also plotted in Figure 2c. The maximal  $\Gamma$  of this work at approximately  $3 \times 10^4$  is also over one order of magnitude higher than that ( $\Gamma = 1328$ ) of the hydrothermal-synthesized  $V_2O_5$  NWs [2]. Compared with other nanostructured semiconductor devices, the  $\Gamma$  of the  $V_2O_5$  NW is higher than those of ZnS NBs ( $\Gamma \sim 0.5 A W^{-1}$ ) [30], ZnSe NBs ( $\Gamma \sim 0.4 A W^{-1}$ ) [31], ZnO nanospheres ( $\Gamma \sim 5 A W^{-1}$ ) [32],  $Nb_2O_5$  NBs ( $\Gamma \sim 6 A W^{-1}$ ) [33], and  $WO_3$  NWs ( $\Gamma \sim 5 \times 10^3 A W^{-1}$ ) [36] and is lower than those of ZnO NWs ( $\Gamma \sim 2 \times 10^8 A W^{-1}$ ) [37],  $SnO_2$  NWs ( $\Gamma \sim 9 \times 10^7 A W^{-1}$ ) [38], GaN NWs ( $\Gamma \sim 10^6 A W^{-1}$ ) [34], and ZnS/ZnO biaxial NBs ( $\Gamma = 2 \times 10^6 A W^{-1}$ ) [35].

In addition, the power-dependent behavior of  $R$  (or  $\Gamma$ ) could imply the potential hole trapping PC mechanism. The unintentionally doped  $V_2O_5$  semiconductor has been confirmed to exhibit n-type conducting [6,22,39]. Under low power density, the photoexcited holes are totally captured by certain defects which function as a hole trap. The hole trapping effect leaves unpaired electrons which exhibit a long lifetime ( $\tau$ ). As photocurrent is linearly dependent on carrier lifetime, i.e.,  $i_p \propto \tau$ , the long-lifetime electron will substantially enhance and

dominate the photocurrent generation. As the  $\tau$  of electron which is decided by the hole trapping time is now a constant,  $R$  (or  $\Gamma$ ) will be independent of the excitation power, i.e.,  $R$  (or  $\Gamma$ ) = const. Once the power exceeds a critical value (trap filling intensity), the photogenerated hole density is much higher than the trap density and the traps will be fully occupied. Under this condition, the trapping effect can be ignored and photocarriers will follow the bimolecular recombination mechanism [40-42]. The recombination after trap filling results in the decrease of  $\tau$  with the increase of  $I$ , making an intensity-dependent  $R$  (or  $\Gamma$ ) following an inverse power law, i.e.,  $R$  (or  $\Gamma$ )  $\propto I^{-k}$ , where the theoretical  $k = 1/2$  [42]. The aforementioned model agrees with the two-stage power-dependent  $R$  (or  $\Gamma$ ) result in Figure 2c and  $i_p$  in Figure 2b. The trap filling intensity is roughly at 5  $W m^{-2}$ , and the fitted  $k$  value is  $0.62 \pm 0.04$  for the  $V_2O_5$  NWs.

The change of recombination behavior can be further verified by the power-dependent  $\tau$  measurement. Figure 3a illustrates the normalized photocurrent rise curves under



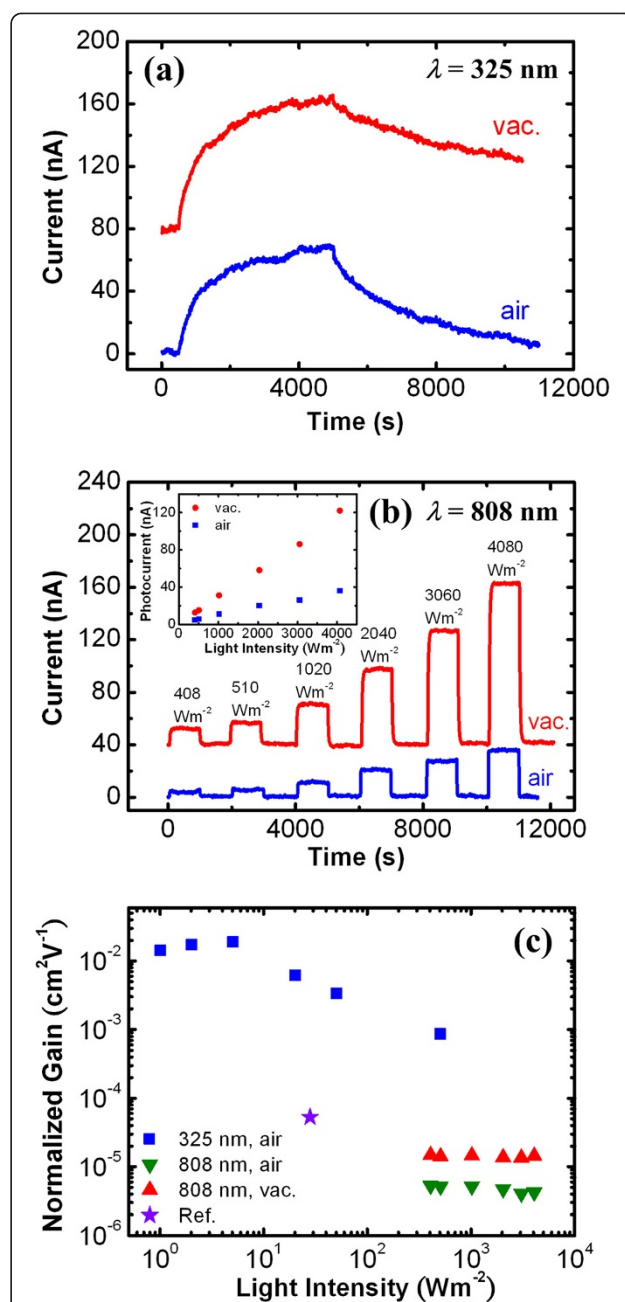
**Figure 3** Normalized photocurrent rise curves and fitted carrier lifetime versus intensity. (a) The normalized photocurrent rise curves under inter-band excitation ( $\lambda = 325$  nm) with selected intensity and (b) fitted carrier lifetime versus intensity measured at a bias of 0.1 V for the  $V_2O_5$  NW with  $d = 800$  nm and  $l = 2.5$   $\mu m$ .

selected light intensity. The result shows that the rise time or photoresponse time increases with the decrease of power density. By fitting the photoresponse curves using stretched exponential function  $i_p(t) = i_{p0} \exp[-(t/\tau)^\beta]$ , where  $i_{p0}$  is the steady-state photocurrent and  $\beta$  is the stretching factor smaller than unity; the dependence of  $\tau$  on power density can be obtained and is depicted in Figure 3b. The result shows that the  $\tau$  also follows the similar two-stage power dependence as  $R$  (or  $\Gamma$ ), which further confirms the lifetime-dominant hole trapping PC mechanism in the  $V_2O_5$  NWs.

According to literature reports, the photoconductivity of metal oxide semiconductor NWs, such as ZnO, SnO<sub>2</sub>, TiO<sub>2</sub>, and WO<sub>3</sub>, mostly follow a common oxygen-sensitized (OS) PC mechanism [36,37,43-45]. The mechanism is controlled by the interaction of foreign oxygen molecule and semiconductor in the near surface area. According to the OS model, the PC process includes four steps: (1) In the dark and in the atmospheric ambience, as oxygen plays a role of electron trap state in the metal oxide semiconductor surface, through oxygen adsorption, the electron is captured on the surface and creates negatively charged surface states (or oxygen ions) [ $O_2(g) + e^- \rightarrow O_2(ad)$ ]. The effect induces an enhanced upward bending of the energy band at the surface. (2) Under light illumination, electron-hole pairs are generated [ $h\nu \rightarrow e^- + h^+$ ] and (3) subsequently separated by the surface electric field or band bending. (4) The excess holes are attracted by the surface and recombine with negative-charged oxygen on the surface [ $h^+ + O_2^-(ad) \rightarrow O_2(g)$ ]. The result leaves unpaired electrons with prolonged lifetimes, which is similar to the hole trapping effect in the bulk. Recombination can only take place when oxygen molecules re-adsorb on the surface as that in step 1.

By the aforementioned mechanism, the recombination rate and lifetime of the excess electron are governed by the oxygen adsorption rate. Therefore, the recombination rate of electrons can be highly reduced, and the  $i_p$  and  $\tau$  can be enhanced while varying the ambience from air (oxygen-rich) to vacuum (oxygen-deficient). The ambience-dependent behavior of PC is the most direct measure to verify the surface-controlled PC mechanism in the metal oxide semiconductors. Accordingly, the environment-dependent photoresponse measurement for the  $V_2O_5$  NWs was also performed. Figure 4a shows that the photoresponse curves measured in air and vacuum ambiances at  $I = 20 \text{ W m}^{-2}$  of the  $V_2O_5$  NW did not reveal any significant difference, which is distinct from the description of the OS mechanism. The  $V_2O_5$  NW without surface effect under inter-band excitation actually is consistent with the bulk-dominant hole trapping mechanism observed by the power dependence study.

Although the photoconductivity of the  $V_2O_5$  NWs has been confirmed to be dominated by the bulk under



**Figure 4** Photoresponse curves under inter- and sub-bandgap excitations and calculated normalized gain versus intensity. (a) The photoresponse curves under inter-bandgap excitation ( $\lambda = 325 \text{ nm}$ ) at  $I = 20 \text{ W m}^{-2}$  in air and vacuum ambiances, (b) the photoresponse curves under sub-bandgap excitation ( $\lambda = 808 \text{ nm}$ ) at increasing  $I$  from 408 to 4,080  $\text{W m}^{-2}$  in air and vacuum ambiances, and (c) the calculated normalized gain versus intensity at  $\lambda = 325$  and 808 nm in air and vacuum ambiances for the  $V_2O_5$  NW with  $d = 800 \text{ nm}$  and  $l = 2.5 \mu\text{m}$ . The insert in (b) shows the photocurrent versus intensity plots at  $\lambda = 808 \text{ nm}$  in air and vacuum.

band-to-band ( $\lambda = 325 \text{ nm}$ ) excitation, the sub-bandgap excitation using the 808-nm wavelength ( $E = 1.53 \text{ eV}$ ) was also carried out to further characterize the layered

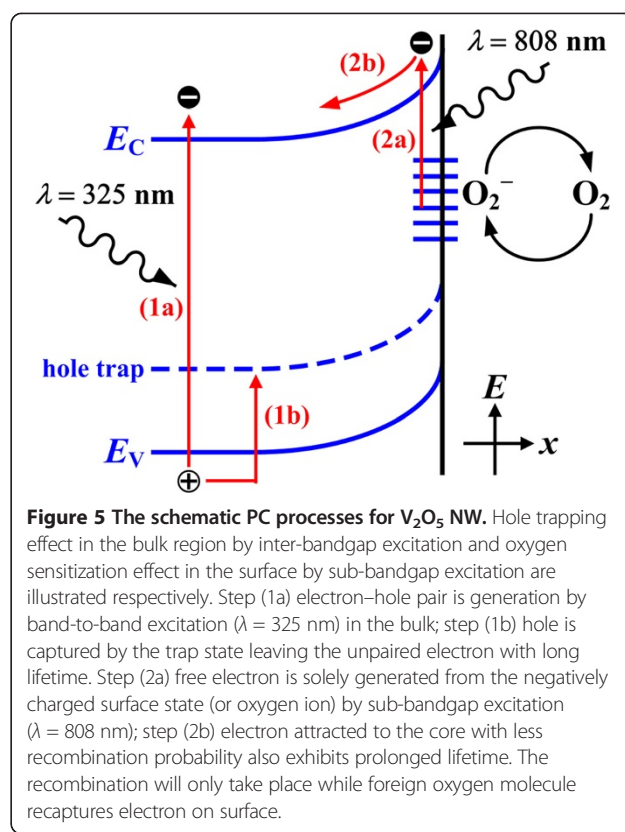
1D nanostructure. Figure 4b depicts the photoresponses under the sub-bandgap light illumination at different  $I$  and at  $V = 0.1$  V in air and vacuum ambiances for the  $V_2O_5$  NW with  $d = 800$  nm and  $l = 2.5$   $\mu$ m. As the values of photoresponse at sub-bandgap excitation are much less than the inter-bandgap excitation, the  $I$  of the 808-nm wavelength was operated at a relatively high range of 408 to 4,080  $W\ m^{-2}$ . Under high-power condition, the sub-bandgap excitation generates an observable photoresponse and the  $i_p$  is linearly dependent on  $I$ . The  $i_p$  versus  $I$  curves in air and vacuum ambiances are also plotted in the inset of Figure 4b. The monotonic linear dependence of  $i_p$  and  $I$  is different from the two-stage power dependence for the band-to-band excitation in Figure 2b, implying the different PC mechanisms. The response time at a few seconds by 808-nm excitation is also much faster than that ( $\tau > 100$  s) by 325-nm excitation.

The more important difference is that the photoresponse under sub-bandgap excitation exhibits clear environment dependence. A similar behavior has also been observed by Tamang et al. [19]. The  $i_p$  in the vacuum is roughly three times higher than that in air. This observation is consistent with the OS mechanism in metal oxide semiconductors. Although the mechanism is usually described by the spatial separation of the electron-hole pair under above-bandgap excitation, the sub-bandgap light that excites electrons from the surface trap state to conduction band could result in a similar effect [46,47]. The schematic PC processes of hole trapping in the bulk and surface state excitations is shown in Figure 5. Although electron transition from the valence band to surface states may also generate a free hole which is able to recombine with oxygen ions and release trapped electrons leading to similar OS effect, the surface states are mostly occupied and negatively charged (i.e., the surface-adsorbed oxygen molecules are mostly ionized). The result indicates that the transition probability is rather low, which allows us to neglect the minor contribution. As light absorption only takes place at the surface, this could explain the very high power that is required to produce an observable photoresponse using the 808-nm excitation source.

To compare the PC efficiencies between the above- and below-bandgap excitations and between the  $V_2O_5$  NWs grown by PVD and hydrothermal approaches, a new photoconductor parameter named normalized gain ( $\Gamma_n$ ) is adopted and discussed [45,48]. As the frequently used  $\Gamma$  is physically defined as the ratio of  $\tau$  to transit time ( $\tau_t$ ) between two electrodes of a device, i.e.,

$$\Gamma = \frac{\tau}{\tau_t}, \text{ and } \tau_t = \frac{l}{v},$$

where  $v$  is the carrier drift velocity which is equal to the product of mobility ( $\mu$ ) and applied electric field ( $F$ ), i.e.,  $v = \mu F$ , where  $F = \frac{V}{l}$ ,  $\Gamma$  can be rewritten as  $\Gamma = \frac{V}{l^2} \tau \mu$  [29].



**Figure 5** The schematic PC processes for  $V_2O_5$  NW. Hole trapping effect in the bulk region by inter-bandgap excitation and oxygen sensitization effect in the surface by sub-bandgap excitation are illustrated respectively. Step (1a) electron-hole pair is generation by band-to-band excitation ( $\lambda = 325$  nm) in the bulk; step (1b) hole is captured by the trap state leaving the unpaired electron with long lifetime. Step (2a) free electron is solely generated from the negatively charged surface state (or oxygen ion) by sub-bandgap excitation ( $\lambda = 808$  nm); step (2b) electron attracted to the core with less recombination probability also exhibits prolonged lifetime. The recombination will only take place while foreign oxygen molecule recaptures electron on surface.

Accordingly,  $\Gamma$  depends on  $l$  and  $V$ . In terms of engineering application, photodetectors can be operated with high  $\Gamma$  by shortening  $l$  and increasing  $V$ . However, to objectively compare the intrinsic PC efficiency of the materials, the artificial factors have to be excluded.

Accordingly, we adopted the  $\Gamma_n$ , physically defined as the product of  $\eta$ ,  $\tau$ , and  $\mu$  (i.e.,  $\Gamma_n = \eta \tau \mu$ ) [45,48]. As the  $\tau \mu$  product is an intrinsic quantity determining photocarrier transport efficiency [42], for a constant  $\eta$ ,  $\Gamma_n$  offers the same physical meaning as  $\tau \mu$ , and its intrinsic property can exclude the effects of device dimension and experimental condition. In addition,  $\Gamma_n$  with the factor of  $\eta$  could take the real light absorption efficiency into account, whose importance has been demonstrated to further understand the PC process in 1D nanostructures [49].  $\Gamma_n$  can be obtained by the following equation [45,48]:

$$\Gamma_n = \Gamma \eta \frac{l^2}{V} = \frac{E i_p l^2}{q P V}. \quad (1)$$

The calculated  $\Gamma_n$  versus  $I$  using the data of  $\Gamma$  (Figure 2c) or  $i_p$  (Figure 2b) for the  $V_2O_5$  NW measured at  $V = 0.1$  V under 325-nm ( $E = 3.82$  eV) and 808-nm ( $E = 1.53$  eV) illuminations are illustrated in Figure 4c. One data point of hydrothermal-synthesized  $V_2O_5$  NWs calculated according to the data in [2] ( $E = 2.76$  eV) is also plotted for comparison.

After excluding the artificial contributions of  $I$  and  $V$ , the  $\Gamma_n$  of our PVD-grown  $V_2O_5$  NWs at approximately  $6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1}$  is two orders of magnitude higher than that ( $\Gamma_n \sim 5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1}$ ) of the hydrothermal-synthesized ones for the similar  $I = 25 \pm 5 \text{ W m}^{-2}$ . This result indicates the PVD-grown NWs exhibit a higher efficiency for photocarrier transport and photocurrent generation than the hydrothermal ones. The PVD (or thermal evaporation) approach usually provides better control for crystal growth, and the growth temperature at  $550^\circ\text{C}$  is also relatively high in comparison with that in the hydrothermal method (synthesis at  $205^\circ\text{C}$ ). Accordingly, it is inferred that the higher PC efficiency (or  $\Gamma_n$ ) originated from a higher crystalline quality in this PVD-grown  $V_2O_5$  nanostructure.

In addition, Figure 4c also shows that the  $\Gamma_n$  at 325-nm excitation is also much higher than that at 808-nm excitation. The optimal (saturation)  $\Gamma_n$  at  $\lambda = 325 \text{ nm}$  is  $1.7 \pm 0.2 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1}$  which is over three orders of magnitude higher than that ( $\Gamma_n = 4.7 \pm 0.6 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1}$ ) at  $\lambda = 808 \text{ nm}$  in air ambience. The  $\Gamma_n$  enhanced in the vacuum can also be observed therein. The analysis quantitatively demonstrates the difference of PC efficiency induced by above- and below-bandgap excitations. As  $\Gamma_n$  linearly depends on  $\eta$  and  $\tau$  and the volume for optical absorption (or  $\eta$ ) of the bulk by inter-bandgap excitation is much higher than that of the surface under sub-bandgap excitation, it is proposed that  $\eta$  plays an important role on the  $\Gamma_n$  difference for the wavelength-dependent PC. The relatively long photoresponse time (or  $\tau$ ) could also contribute to the higher  $\Gamma_n$  under inter-bandgap (325 nm) excitation.

Finally, it is noted that the PC mechanism based on the small polaron hopping transport has been proposed by Lu et al. [21]. The very short lifetimes in the range of 1 to 1,000  $\mu\text{s}$  are usually one of the criteria to manifest the polaron hopping mechanism. However, the typical lifetimes in this study either under 325 or under 808 excitation are at the orders of magnitude from seconds to hundred seconds, which is at least three orders of magnitude higher than the relaxation time of small polaron. The substantial difference could allow us to explain the PC mechanism on the basis of the conventional band conduction model (as shown in Figure 5) for monocrystalline semiconductors. The free electron-dominant conduction mechanism could also offer a probable explanation for the relatively higher  $\sigma$  in the PVD-grown  $V_2O_5$  NWs in comparison with the literature data of which hopping is the dominant factor for charge conduction [23,24].

## Conclusions

Photoconductivities of the PVD-grown  $V_2O_5$  NWs with monocrystalline orthorhombic structure have been investigated. In addition to the device performance, the

PVD-grown  $V_2O_5$  NWs exhibit two orders of magnitude higher PC efficiency (or  $\Gamma_n$ ) than their hydrothermal-synthesized counterparts. In addition, the PC mechanism has also been studied by the power, environment, and wavelength-dependent measurements. Both the bulk-controlled (hole trapping effect) and surface-controlled (oxygen-sensitization effect) PC mechanisms have been observed under above- and below-bandgap excitations, respectively. Understanding of the transport properties in this layered  $V_2O_5$  1D nanostructure could enable us to design the electronic, optoelectronic, and electrochemical devices by a more efficient way.

## Competing interests

The authors declare that they have no competing interests.

## Authors' contributions

RSC designed the experiments, analyzed the data, proposed the model, and drafted the manuscript. WCW and CHC carried out experimental measurements. HPH participated in the result discussion. LCT and YJC carried out material growth. All authors read and approved the final manuscript.

## Acknowledgements

Ruei-San Chen would like to thank the financial support of the Taiwan National Science Council (grant nos. NSC 99-2112-M-011-001-MY3 and NSC 99-2738-M-011-001) and the National Taiwan University of Science and Technology (NTUST).

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Received: 7 September 2013 Accepted: 12 October 2013

Published: 25 October 2013

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doi:10.1186/1556-276X-8-443

**Cite this article as:** Chen et al.: Photoconductivities in monocrystalline layered V<sub>2</sub>O<sub>5</sub> nanowires grown by physical vapor deposition. *Nanoscale Research Letters* 2013 **8**:443.

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