Expeditious UV detection of tungstite ($\text{WO}_3 \cdot \text{H}_2\text{O}$) and tungsten oxide (WO_3) decorated multiwall carbon nanotubes (MWCNT) based photodetector: ultrafast response and recovery time

Rahul Majumder¹ · Soumalya Kundu¹ · Ria Ghosh¹ · Monalisa Pradhan¹ · Dibyendu Ghosh² · Shubham Roy³ · Subhadip Roy⁴ · Manish Pal Chowdhury¹

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Abstract

Tungstite ($\text{WO}_3 \cdot \text{H}_2\text{O}$) and tungsten oxide (WO_3) decorated multi-walled carbon nanotube (MWCNT) based ultra-fast UV photodetectors were fabricated and characterized in this work. Tungstite was synthesized by wet chemical route and tungsten oxide was derived by calcinating tungstite at elevated temperatures (723 K and 1023 K). The crystal structures of tungstite and tungsten oxide were confirmed from X-ray diffraction analysis. The UV photo responsive behavior of the tungstite and tungsten oxide decorated MWCNT UV photodetectors were studied using 365 nm UV LED array in the intensity range $15\text{--}83 \mu\text{W cm}^{-2}$. The device showed good UV photoresponsivity with high external quantum efficiency (EQE). Tungstite decorated MWCNT UV photodetector exhibited maximum responsivity of 7.4 AW^{-1} along with EQE of 2550% under the incident UV intensity of $15 \mu\text{W cm}^{-2}$. Up to 500 Hz optical chopping frequency, the devices showed remarkable stability along with good repeatability of UV detection. Response and recovery time is recorded as low as 400 μs and 500 μs respectively for tungstite decorated UV photodetectors.

Keywords MWCNT · Tungstite · Tungsten oxide · UV photodetector · Response time · Recovery time

1 Introduction

In the past decade, intensive research has focused on carbon nanotubes (CNT) due to its unique electrical, thermal and mechanical properties. CNTs are cylindrical tubes made of rolled-up sheet of single layer of carbon atoms (graphene) with typical diameter in nanometers. It can be synthesized by electrical arc discharge, laser ablation method and chemical vapor deposition (CVD) methods [1–3]. CNTs can be divided in three different categories depending upon the number of walls, single-walled CNT and multi-walled CNT (MWCNT). MWCNT has potential

application in electrochemical devices, field emission devices, nano electronic devices, sensors [4–6] etc. Exposure to ultra-violet (UV) radiation can do serious damage to human and other living beings. From this point of view, UV photodetectors have an important role in health care. Even in commercial applications, such as space-to-space communications, flame sensing, pollution monitoring and water sterilization UV photodetectors are used extensively [7]. Though ZnO, GaN and In_2O_3 are used in UV photodetectors, there are few reports on tungsten oxide (WO_3) as UV photodetectors [7–11]. Oxygen vacancies, oxygen absorption–desorption and electron–hole recombination

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✉ Manish Pal Chowdhury, manishpc@gmail.com | ¹Department of Physics, IEST Shibpur, Howrah, West Bengal 711103, India. ²Department of Materials Science, IACS, Kolkata 700032, India. ³Department of Physics, University of Jadavpur, Kolkata 700032, India. ⁴Department of Physical Science, IISER Kolkata, Mohanpur, West Bengal 741246, India.

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phenomena near the surface of tungsten oxide contribute towards its photoconductive activity. In the present work, we report on fabrication and characterization of tungstite ($\text{WO}_3 \cdot \text{H}_2\text{O}$) and tungsten oxide decorated MWCNT based UV photodetectors. Tungstite and tungsten oxide were used as UV photoresponsive material and MWCNT network was exploited as the carrier of the photocurrent.

2 Materials and methods

2.1 Growth of MWCNT

MWCNT were grown on 300 nm oxidized silicon wafer using catalytic thermal chemical vapour deposition (CVD) technique. Oxidized silicon wafer was cleaned by using ultrasonication in acetone followed by vapour degreasing in hot iso-propanol. The catalyst solution was prepared by dissolving 50 mg ferric nitrate ($\text{Fe}(\text{NO}_3)_3$) in 10 ml ethanol. The solution was stirred with magnetic stirrer for 15 min at room temperature. A thin layer of catalyst seed layer was spin-coated on the oxidized silicon wafer at 1000 rpm for 60 s. The substrate was dried on a hot plate at 373 K for 5 min. The growth process was divided in three steps and carried out in a split open tube furnace. First step involved oxidation of the catalyst layer at 973 K in air for 10 min. In second step the catalyst layer was reduced at 1023 K in the continuous flow of hydrogen (H_2) at 0.4 SLPM for 7 min. Finally, MWCNTs were grown on the reduced catalyst layer. After reduction, the chamber was flushed with argon (Ar) flow at 0.2 SLPM and maintained in Ar atmosphere until the growth temperature was increased to 1173 K. At this point flow of Ar, H_2 and C_2H_2 were maintained at 0.6, 0.4 and 0.05 SLPM respectively. To reduce the presence of amorphous carbon, Ar gas was passed through water bubbler during growth at room temperature. The growth process was continued for 15 min at 1173 K. At the end, the chamber was taken out of the furnace and cooled to room temperature in 0.2 SLPM Ar flow.

2.2 Synthesis of tungstite and tungsten oxide

Tungsten oxide was prepared from sodium tungstate (Na_2WO_4) by solution based method as reported by Chai et al. [12]. 10 ml precursor solution of 0.15 M concentration was prepared in de-ionised water, followed by 30 min stirring with magnetic stirrer at 2000 rpm. 3.75 ml of nitric acid solution (3 M) was added drop-wise to the precursor solution under continuous stirring. Then the solution was stirred at 1500 rpm for 90 min before it was left for aging. Formations of tungstite and tungsten oxide are explained with the following reactions.

$\text{WO}_3 \cdot x\text{H}_2\text{O}$ was synthesized by oxidizing of Na_2WO_4 and the value of 'x' depends upon the degree of ionization of the solution. Adhikari et al. [13] proposed and confirmed the transformation of tungsten oxide from tungstite as explained in reaction 2 and 3 [13]. The solution was centrifuged at 5000 rpm for 10 min to separate the yellow precipitate (reaction 2). The precipitate was cleaned with de-ionized water and methanol repeatedly three times to remove residual chemicals. The precipitate was dried at 373 K and calcinated at 773 K and 1023 K to produce orthorhombic tungstite, monoclinic and mixed-phase tungsten oxide powder respectively. The three samples are noted as TO1, TO2 and TO3 respectively in the paper.

2.3 Characterization

Microstructural properties were investigated using FE-SEM (INSPECT F50, Netherland). Tungstite (TO1) and two tungsten oxide (TO2 and TO3) samples were characterised with Panalytical X-ray diffractometer (PW 3040/60). Optical properties are studied with Horiba T64000 Raman spectrometer (532 nm laser excitation at 2 mW/cm² intensity). Kiethley A-221A-3 voltage source was used to apply bias voltage to the UV photodetectors and photo response current was measured using SRS 570 preamplifier and DAQ.

3 Result and discussion

3.1 Characterization of MWCNTs

FE-SEM image of the MWCNT grown by CVD technique is shown in Fig. 1a. Uniform growth of MWCNT network can be observed throughout the substrate. Raman spectroscopy data of the MWCNT display D and G peaks at 1350 cm⁻¹ and 1590 cm⁻¹, as shown in Fig. 1b. The intensity ratio ($I_D/I_G < 100$) of D and G peaks suggest growth of MWCNTs [14]. From Fig. 1b it can be observed that the ratio of intensity of D (I_D) and G (I_G) peaks is > 1 , indicating the presence of defects in the MWCNTs [14].

3.2 Characterization of $\text{WO}_3 \cdot \text{H}_2\text{O}$ and WO_3

Surface morphology of the tungstite and tungsten oxide (TO1, TO2 and TO3) samples are shown in Fig. 2a–c. In the case of TO1, dried at 373 K, cuboid structures were

Fig. 1 **a** FESEM image of MWCNT. **b** Raman spectra of MWCNT

Fig. 2 FESEM images of **a** TO1, **b** TO2 and **c** TO3 powders. Scale bars correspond to 3 μm

observed. Similar cuboid particles are also observed in case of TO2. For the sample TO3, calcinated at 1023 K, large deformed particles formed due to agglomeration.

X-ray diffraction (XRD) data of tungstite and tungsten oxide are shown in Fig. 3a. X-ray reflection from (020), (111) planes are observed at 16.45° , 25.57° , which are the prominent planes of tungstite ($\text{WO}_3 \cdot \text{H}_2\text{O}$). Three weak peaks of tungstite are also observed at 34.1° , 34.95° , 49.17° corresponds to (200), (002) and (042) planes respectively. The XRD data is in confirmation with the results reported by Miao et al. (JCPDS card no. 43-0679) [10]. The X-ray diffraction pattern indicates the formation of polycrystalline tungstite orthorhombic crystal, with good crystallinity along (002) and (111) planes. For sample TO2 predominant peak at 23.02° is observed along with several small peaks at 23.5° , 24.23° , 28.61° and 33.53° . TO2 is identified as the monoclinic phase of tungsten oxide (JCPDS no. 83-0951) [15]. The predominant peak at 23.02° is originated from the reflection from (002) planes whereas the weaker peaks represent (020), (200), (112) and (022) planes respectively. In sample TO3 all signature peaks of monoclinic are observed along with five smaller peaks at 26.48° , 35.33° ,

47.17° , 48.56° and 55.68° . The peaks at 26.48° , 35.33° and 55.68° correspond to reflection from (120), (202) and (420) planes respectively. These three above mentioned peaks are observed for both monoclinic and orthorhombic WO_3 , but the peaks at 47.17° and 48.56° are the reflection from (004) and (104) planes of orthorhombic WO_3 (JCPDS 20-1324) [16].

Raman spectra of the three samples are shown in Fig. 3b. In the case of TO1, single broad peak and a single sharp peak are observed at 632 cm^{-1} and 944 cm^{-1} respectively. According to Ng et al. [17], transition metal oxides display sharp Raman peak in the range $950\text{--}1050\text{ cm}^{-1}$, which denotes the stretching of the metal–oxygen ($\text{W}=\text{O}$) double bond. For TO1, similar peak is observed at 944 cm^{-1} , and the broad peaks at 632 cm^{-1} is due to the vibration of $\text{W}-\text{O}$ bond. The $\text{W}-\text{O}$ bond is weaker from the $\text{W}=\text{O}$, so the vibration is observed in the lower range. The peaks in between the range from 180 to 250 cm^{-1} occurs due to the stretching, bending or deformation of $\text{O}-\text{W}-\text{O}$ as observed at 193 cm^{-1} and 230 cm^{-1} in TO1. In case of sample TO2 and TO3, the peaks at 713.8 cm^{-1} and 805.7 cm^{-1} are assigned to ($\text{O}-\text{W}-\text{O}$) stretching vibration

Fig. 3 **a** X-ray diffraction pattern and **b** Raman spectra of the three samples (TO1, TO2 and TO3)

Fig. 4 Schematic of metal oxide decorated MWCNT UV photodetector

whereas the peak at 271.6 cm^{-1} is due to the (W–O–W) deformation vibration [18–20]. The peaks are observed for both hexagonal and monoclinic WO_3 , but the peak 133.0 cm^{-1} correspond to the monoclinic WO_3 [21].

3.3 UV photodetection characterization

The UV photodetector was fabricated by drawing silver (Ag) paste electrodes on the MWCNTs. Followed by drop casting of freshly sonicated TO1, TO2 and TO3 dispersed ethanol solutions in the area between two Ag electrodes. The schematic of the UV photodetector is shown in Fig. 4.

I–V characteristics of TO1 decorated MWCNT UV photodetector, at 1.0 V bias, is presented in Fig. 5a. The

Fig. 5 **a** I–V characteristics of TO1 decorated MWCNT device under $15\text{ }\mu\text{W cm}^{-2}$ UV intensity at 1.0 V bias. **b** Time-resolved photocurrent of TO1 decorated MWCNT device in response to the on/off switching of $83\text{ }\mu\text{W cm}^{-2}$ UV

measurements were conducted in dark condition and under the UV illumination of 365 nm UV LED array at $15 \mu\text{W cm}^{-2}$ intensity. In Fig. 5b, the repeatability plot is shown for TO1 decorated UV photodetector. The repeatability measurement was performed under $83 \mu\text{W cm}^{-2}$ UV exposure and in dark, 5 s each. It is clearly seen from the plot that the UV photodetection is highly reproducible and the saturation of the photocurrent remained stable over the entire loop.

As shown in Fig. 6a, the photocurrent (I_{ph}) of the UV detectors increased with UV intensity, varied from 15 to $83 \mu\text{W cm}^{-2}$. Photocurrent of a photodetector is measured from the difference between dark current (I_{dark}) and light current (I_{light}). Maximum photocurrent of $21.9 \mu\text{A}$, $18.7 \mu\text{A}$ and $4.1 \mu\text{A}$ are obtained under UV illumination of $83 \mu\text{W cm}^{-2}$ for TO1, TO2 and TO3 decorated devices respectively. The measured photocurrents for the devices are much higher than the previously reported WO_3 UV photodetectors [7–9]. In Fig. 6a, the photocurrent–UV intensity plot is fitted according to the following relation [22].

$$I_{ph} \propto P^\theta \quad (4)$$

where P is the power of the incident UV and the response of the photocurrent to the corresponding UV light intensity is determined by θ . The response (θ) of the TO1, TO2 and TO3 decorated devices are 0.28, 0.57 and 0.67 respectively. In case of TO1 decorated MWCNT device the response value is < 0.5 , indicating presence of the traps at the interface [23]. Trapping and recombination of photo generated carriers and complex process of electron–hole generation yield the response (θ) between 0.5 and 1, as obtained for the TO2 and TO3 decorated UV photodetectors [22]. The responsive behavior of different devices are shown in Fig. 6b. The responsivity (R_i) of the UV photodetector is measured from the photo current (I_{ph}) and the

illumination power over the effective UV detection area (P_{opt}), using the following equation [24, 25],

$$R_i = \frac{I_{ph}}{P_{opt}} \quad (5)$$

For TO1 and TO2 decorated devices, maximum responsivities are 7.4 AW^{-1} and 4.1 AW^{-1} respectively. The responsivity of the devices is similar to the results reported by other researchers [7, 9]. As compared to the other two devices, TO3/MWCNT photodetector show lower responsivity of 0.6 AW^{-1} .

In Fig. 6c the photoconductive gain with respect to UV intensities is plotted for the three UV photodetectors. The ratio of photogenerated charge carriers against the number of absorbed photon by the photoactive material is defined as photoconductive gain [26]. The photoconductive gain and external quantum efficiency (EQE) are expressed by the following equations,

$$\text{Gain} = \frac{I_{ph}/q}{P_{opt}/h\nu} = \frac{R_i}{q/h\nu} \quad (6)$$

$$\text{EQE} = \frac{R_i}{q/h\nu} \times 100\% \quad (7)$$

where q is the electronic charge, h is the Planck constant and ν is the absorbed photon frequency. Maximum photoconductive gain of 25.5 (2550%), 13.97 (1397%) and 2.05 (205%) are calculated for the TO1, TO2 and TO3 decorated MWCNT UV photodetector respectively under the $83 \mu\text{W cm}^{-2}$ UV. The presence of traps and its contribution is explained by the power law fit in photocurrent and UV intensity plot shown in Fig. 6c. Under high UV light intensity, due to hole-trap saturation the devices showed lower EQE compared to the device under the low UV intensity.

Fig. 6 **a** Photocurrent response against the UV intensity (fitted with $I_{ph} \propto P^\theta$), **b** UV intensity dependent responsivity behavior and **c** Variation of EQE (%) along UV intensity (Fitted with power law) for TO1, TO2 and TO3 decorated MWCNT device

The ability of a device to follow a fast varying optical signal is defined as the response speed of a photodetector. To measure the response speed of the UV photodetector, an optical chopper is used to switch the incident light on the device and the response was recorded using an oscilloscope. The photocurrent responses of the TO1 UV photodetector under different chopping frequencies, varied from 100 to 500 Hz, are shown in Fig. 7. Transient photocurrent measurement process of the UV photodetectors is described in the supplementary information. The device showed saturated ultrafast response under all the measured frequency. Even at the higher frequency of 500 Hz, the UV photodetectors showed remarkable reproducibility without any sign of cut-offs. Transient photoresponse, ultra-small response time and recovery time for the devices are presented in Fig. 8. The response time (t_r) is defined as the time taken to increase the photocurrent from 10% to 90% of the maximum photocurrent under the exposure of UV light and the time needed for the photocurrent to decay from 90% of the maximum value to the 10% is denoted as the recovery time (t_d) [7, 9].

For TO1 decorated device the response and recovery time is calculated as low as 400 μ s and 500 μ s respectively which are much smaller than the values reported by Shao et al. [8]. They reported recovery and response time of 13 ms and 16 ms respectively for WO₃ nanodisc/rGO UV photodetector devices [8]. Even compare to the other reported results of tungsten oxide UV photodetectors [7, 9], TO2 and TO3 devices had shown superior recovery time of 448 μ s and 520 μ s and response time of 504 μ s and 540 μ s respectively. A comparative study of response time, recovery time and other parameters is conducted between the present work and the previously reported

Fig. 7 Ultra-fast response of TO1 decorated MWCNT photodetector at optical chopper frequency of **a** 100 Hz, **b** 200 Hz, **c** 300 Hz, **d** 400 Hz, **e** 500 Hz

Fig. 8 Response and recovery time of TO1, TO2 and TO3 decorated MWCNT UV photodetector

for WO₃, ZnO, InAs and TiO₂ UV photodetectors, as shown in Table 1.

3.4 UV detection mechanism

UV activated charge generation mechanism of metal oxide (WO₃ and WO₃·H₂O) is shown in Fig. 9a. In the dark environment the surface of the photoactive material absorb oxygen molecules by capturing free electrons from the metal oxide nanostructure, thereby creating a negatively charged oxygen ion layer over the surface [$O_2(g) + e^- \rightarrow O_2^-(ad)$]. Due to incomplete oxidation and imperfect crystallization, surface oxygen vacancies are common in the metal oxide nano particles and these vacancy sites act as oxygen absorption centers [8]. Due to oxygen absorption a depletion region is formed along the surface of the metal oxide. Upon UV illumination electron–hole pairs are generated in the bulk of metal oxides. The UV generated carriers (holes) moved to the surface of the nano structure and recombine with the negatively charged oxygen ions [$h^+ + O_2^-(ad) \rightarrow O_2(g)$]. The recombination increases the number free charges on the surface of photoactive material, thereby increasing the photocurrent in the metal oxide [8, 31–33].

Ultrafast response of the tungstite and tungsten oxide decorated MWCNT UV photo detectors are explained in Fig. 9b, c. The electron affinity (EA) of the molecule, as determined by several process, such as, photodetachment threshold, charge transfer threshold, flame equilibrium etc., lies in the range 3.2–4.0 eV [8, 34]. Work function of MWCNT is reported to be ~4.53 eV [35]. The EA of the metal oxide is lower than the work function of MWCNT, so the UV generated free electrons move from the surface of

Table 1 Comparison of photoconduction parameters

Device	Photocurrent	Responsivity AW^{-1}	EQE (%)	Rise/decay time	References
3D WO_3 nanoshell	4.5 μA	5.1	1678	6.3 s/0.5 s	[7]
WO_3 nanowire on carbon paper	0.6 μA	–	–	3 s/20 s	[9]
WO_3 nanodisc/rGO	1.15 μA	6.4	–	13 ms/16 ms	[8]
WO_3 polycrystal nanobelt	12 nA	2.6×10^5	8.1×10^7	–	[27]
Colloidal ZnO nanoparticle	~ 50 μA	61	–	< 0.1 s/1 s	[28]
TiO_2 nanowire array	15.2 μA	0.17	60.7	–	[29]
InAs nanowire	~ 34.2 nA	4.4×10^3	–	–	[30]
$\text{WO}_3 \cdot \text{H}_2\text{O}$ decorated MWCNT	21.9 μA	7.4	2550	400 μs /500 μs	This work
WO_3 decorated MWCNT	18.9 μA	4.1	1397	448 μs /504 μs	This work

Fig. 9 **a** Photoconduction mechanism of tungstite and tungsten oxide decorated MWCNT UV photodetector. **b** Energy band diagram of the photodetectors. **c** Schematic of carrier transport between photoactive particles and MWCNT

the WO_3 to the MWCNT very easily. In case of the conductivity and the carrier mobility, the MWCNT is much superior to metal oxide, resulting faster charge transportation through the device. Faster charge transport through the MWCNT contributes to the expeditious UV photodetection of the tungstite and tungsten oxide decorated MWCNT UV photodetectors.

4 Conclusion

Ultrafast UV photodetectors were fabricated using tungstite and tungsten oxide decorated MWCNTs. Orthorhombic tungstite, monoclinic and mixed phase tungsten oxide were synthesized by varying the calcination temperatures and verified from the XRD analysis and Raman spectroscopy. Under $15 \mu\text{W cm}^{-2}$ UV intensity, orthorhombic tungstite decorated MWCNT UV photodetector exhibited

maximum responsivity of 7.4 AW^{-1} , whereas monoclinic and mixed phase MWCNT decorated device showed 4.1 AW^{-1} and 0.6 AW^{-1} respectively. The UV photogenerated carrier transportation through the MWCNT contributed to the ultrafast response and recovery of the UV photodetectors. Even under the high frequency optical chopper the devices showed remarkable stability and repeatability. The response and recovery time is recorded as low as 400 μs and 500 μs for tungstite decorated MWCNT photodetector.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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