HIGH PERFORMANCE FLEXBILE ULTRAVIOLET PHOTODETECTORS BASED ON TiO_2/GRAPHENE HYBRID

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ABSTRACT

This paper reports a novel ultraviolet (UV) photodetector based on TiO_2/Graphene hybrid, with high responsivity (0.304A/W) which is ~100 times higher than that based on pure TiO_2. In the hybrid material, Graphene brings two major benefits: (1) large surface area to load sufficient TiO_2 nanoparticles, (2) the generated electrons are instantly collected due to the prominent electrical properties of Graphene which can overcome the low quantum efficiency of pristine TiO_2 caused by recombination of electron-hole pairs. Thus, the collaboration of TiO_2 and Graphene contributes to the high performance of the device. Moreover, this device is fabricated on a flexible substrate using a facile spraying method which lights the possibility to broaden the future of photodetectors in wearable devices.

INTRODUCTION

Photodetectors are devices that convert an optical signal into an electrical signal, and are important components for various applications. Corresponding to 3 different wavelength regions, there are photodetectors for UV, visible and infrared illumination. UV photodetectors can detect light with specific wavelength in the UV region (100~400nm) and have drawn extensive attention owing to their applications in fields such as medicine, military defense, flame detection and space communications. In these applications, high responsivity, fast response time, and good signal-to-noise ratio are common desirable characteristics [1]. Usually wide bandgap semiconductors are chosen as materials for UV photodetectors because electrons will be excited only when they accept photons whose energy are larger than bandgap. The bandgap of UV-sensitive materials should be big enough to distinguish UV light from visible light.

In recent years, many researchers attempt to explore UV photodetectors based on materials such as GaN, SiC and metal oxides. As one of the metal oxides that gives rise to continuous research interest, TiO_2 is a wide bandgap semiconductor (3.2eV), which is highly photo-active when under illumination of an UV light with photon energy larger than its bandgap [2]. Ever since its first appearance for water photolysis by Fujishima and Honda in 1972 [3], TiO_2 has attracted considerable interest in many applications such as dye-sensitized solar cells, water splitting and photodetectors fields [4]. TiO_2 is abundant in mineral storage, chemically stable, low-cost and non-toxic, thus has been proven to be one of the most promising materials for UV photodetectors. For the past decade, significant progress has been made in improving the performance of TiO_2-based UV photodetectors and many mature methods have been developed to easily deposit TiO_2 films, which include RF magnetron sputtering [5], hydrothermal synthesis [6], sol-gel spin-coating [7] and etc.

However, pristine TiO_2 suffers the problem of low quantum efficiency because free electrons have a long path to travel before they reach the grain boundary and are collected by the electrode. During the travel, a free electron will lose its energy and freedom, and return to the valence band. An obvious solution is to synthesize nanoscale TiO_2 in which free electrons have much shorter distance to travel before they reach the particle surface and are collected by the electrode. Almost all related modern researches are established upon the nanomaterial science of TiO_2. Further efforts have been made such as shaping the material into one dimensional nanostructures (nanotubes, nanowires or nanofibers) [8-11], or doping with other assisting materials or elements [12, 13].

Up to date, few reports mention a solution to efficiently collect the photo-generated free electrons in order to enhance the performance of TiO_2-based photodetectors. In this work, we develop a novel photodetector based on TiO_2/Graphene hybrid. The hybrid material is mainly composed of Graphene sheets, decorated with TiO_2 nanoparticles. Upon UV illumination, the electrons in TiO_2 will transit from the valence band into the conduction band and create an electron-hole pair. Graphene sheets can rapidly separate electron-hole pairs, collect the photo generated electrons and enlarge the photocurrent by up to one hundred times. Compared with conventional devices based on pure TiO_2, the joint collaboration of TiO_2 and Graphene can significantly enhance the photodetector performance and also contributes to the fast response. With the assistance of a spray pistol driven by nitrogen flow, the hybrid material is sprayed onto an interdigital Au electrode, which is micro patterned on flexible Parylene-C substrate. Additionally, the flexible photodetector can be attached to any available surface and still exhibit good responsivity and repeatability.

CONCEPTION AND FABRICATION

TiO_2 is a universally accepted potential candidate for UV-sensitive material but with a low quantum efficiency due to the recombination of photo-excited electron-hole pairs, which is a major defect. In our research, we manage to modify TiO_2 with Graphene material, which is well-known for its excellent electrical properties. By synthesis of TiO_2/Graphene hybrid, a high performance UV photodetector is fabricated with about 100 times performance enhancement.

The UV photodetector, which composes of an interdigital Au electrode and material layer, is fabricated on the flexible Parylene-C substrate, as shown in Fig.1 (a). Being the core of the device, the concept of TiO_2/Graphene hybrid is shown in Fig.1 (b). In the hybrid material, two dimensional Graphene sheet provides large surface area to load sufficient TiO_2 nanoparticles. When the TiO_2 nanoparticles generate electron-hole pairs upon incident

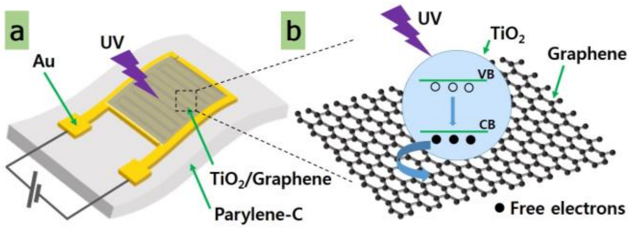

Figure 1: (a) Schematic diagram of a flexible UV photodetector; (b) Charge transfer between TiO_2 and Graphene in TiO_2 coated Graphene sheet.

UV illumination, electrons will be instantly transferred into the Graphene network instead of combining with holes. These electrons 'survive' with the assistance of Graphene and outputs a larger photocurrent than normal.

Following this thought, the fabrication method is shown in Fig.2. Commercially purchased anatase phase TiO_2 and GO powder are dispersed in DI water and ultra-sonicated respectively and then mixed together through magnetic stirring to obtain a homogeneous TiO_2/GO solution. The weight ratio of GO is controlled to be 10%. In the TiO_2/GO solution, TiO_2 can form robust bonding with the functional groups on GO while Graphene sheets don't possess the necessary bonding sites to grasp TiO_2 nanoparticles and can't be easily processed in the solution due to its hydrophobicity. Firstly, 10μm of Parylene-C is deposited on silicon substrate using MOCVD as the flexible base of the device. Then interdigital Au electrode

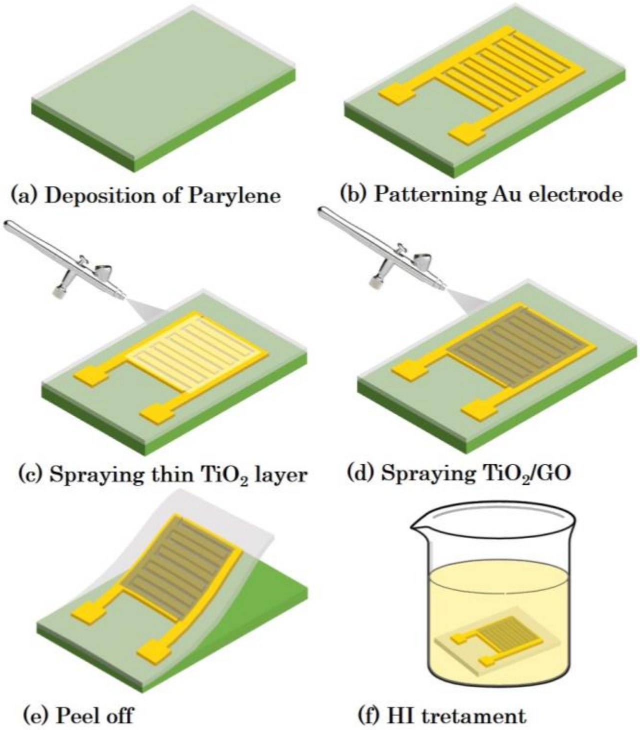

Figure 2: Device fabrication process: (a) MOCVD deposition of 10μm Parylene-C on silicon substrate; (b) Micro pattering Au interdigital electrode; (c) Spray a thin layer of TiO_2 ; (d) Spraying of TiO_2/GO solution; (e) Peel off from the substrate; (f) Immersed in HI to reduce TiO_2/GO to TiO_2/Graphene.

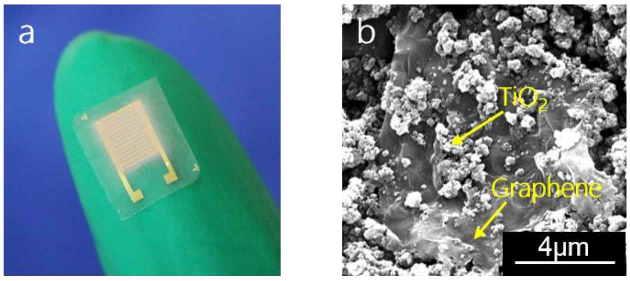

*Figure 3: **(a)** The photo of a flexible UV photodetector; **(b)** SEM image of TiO_2 coated Graphene sheet.*

is patterned using photolithography to form electrical contact and pre-sprayed with a thin layer of TiO_2. After TiO_2/GO is sprayed onto the Au electrode, the device is peeled off from the substrate and immersed in HI for 5 minutes. HI is a strong reductant frequently used in Graphene reduction researches [14], it can remove almost all the functional groups such as hydroxyl, carboxyl and epoxy, and restore the conductive two dimensional Graphene network which consists of single layer carbon atoms. After reduction the device is collected from the HI, rinsed with DI water and dried in vacuum oven at 120℃ for 1h. The photo of the fabricated device, with the size of 10mm×10mm which is tiny enough to stand on fingertip, is shown in Fig.3 (a). From the SEM image of the hybrid material, shown in Fig.3 (b), we can see that Graphene sheet is spread as the background and TiO_2 nanoparticles are uniformly decorated on the sheet, which verifies the initial conception of the hybrid material.

RESULTS AND DISCUSSIONS

Photodetectors with higher responsivity and faster response are more preferable. Responsivity is defined as photocurrent generated under per unit UV illumination energy and response time is defined as the time needed to react to the on/off switch of UV illumination.

The experiments of the photodetectors are performed using an electrochemical workstation. In a typical test, a certain bias or scan voltage is applied to the device and the data is recorded by the workstation. A 20W UV sterilization lamp is used as the UV illumination source and the irradiation intensity is tuned to 20μW/cm^2 by controlling the distance between the lamp and the device. The effective area of the device is 5mm×5mm, 0.25 cm^2. As comparison, photodetectors based on pure TiO_2 are also fabricated with similar processes as control group against the hybrid material. To optimize the UV-sensitive material layer, different material layer thicknesses are studied in a group of 1μm, 2μm and 3μm by controlling the amount of sprayed solution. Thicker TiO_2 film exhibits better conductivity because defect sites will block the conductive paths of electrons while in a thicker film the electrons have more choices to bypass the defect sites, and also higher responsivity due to abundant sensitive materials. In short, thicker film will cause both higher dark current and higher photocurrent. For an advanced photodetector application, the dark current, which is considered as the background noise, is expected to be as low as possible while the photocurrent to be as high as possible. To solve this contradictive bargain, I-V curves of different thicknesses

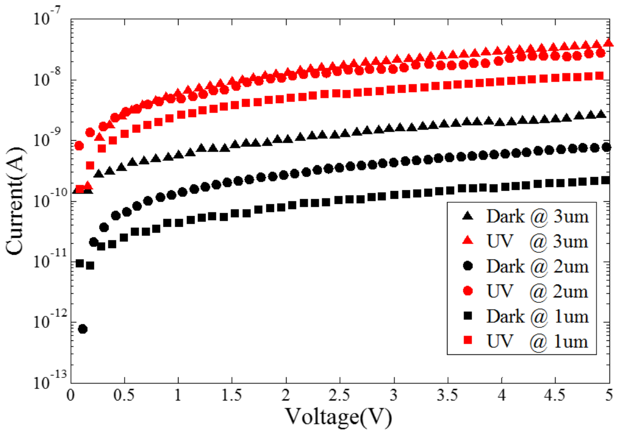

Figure 4: I-V characteristics of a flexible UV photodetector based on pure TiO_2 with different layer thickness measured in dark and under $20\mu W/cm^2$ UV illumination.

are measured in dark and under $20\mu W/cm^2$ UV illumination, as shown in Fig.4. The three red lines and black lines represent tests under UV illumination and in dark respectively while different marker shapes (triangle, square, and dot) represent different film thicknesses. The curves show that, at a certain bias, dark current and photocurrent both increase as the layer becomes thicker. According to the ratio of photocurrent to dark current, we select 2μm as an optimal parameter, which achieves responsivity of 2.6mA/W at 3V bias.

Then we fabricate the device based on TiO_2/Graphene with thickness of 2μm and measure the I-V curves under same conditions as previous, shown in Fig.5. We can see that responsivity enhances after introducing GO and further improves after GO reduction, reaching 0.304A/W. GO is a derivative of Graphene with many functional groups, so its carbon network is similar with Graphene. Thus GO, to a certain extent, also has the ability to capture electrons and separate electron-hole pairs.

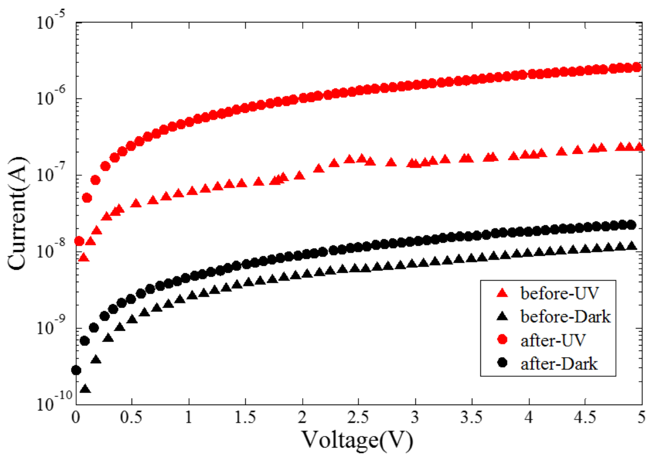

Figure 5: I-V characteristics of a photodetector based on TiO_2/G before and after HI treatment measured in dark and under $20\mu W/cm^2$ UV illumination.

Devices with GO or Graphene content are both fabricated and tested for comparison. TiO_2/Graphene material shows higher conductivity which leads to higher dark current, certainly not desired, but this drawback is compensated by the restored carbon network which boosts the photocurrent, thus the increased dark current noise is negligible. The photocurrent can even reach 1.52μA at 3V bias which is suitable for further read-out circuitry because nA level current would require amplifiers with ultra-high precision and this would pose serious problems upon subsequent read-out design for an actual application.

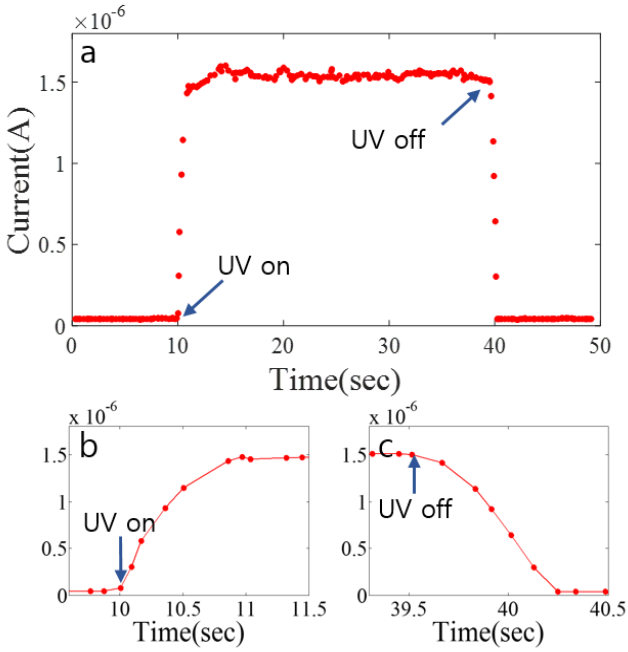

Figure 6: Time response of the flexible UV photodetector. (a) Photocurrent response under on/off switch of $20\mu W/cm^2$ UV illumination at 3V bias; (b) Magnified rise and (c) recovery edges of the photocurrent response.

Responsivity is an important factor for photodetectors because it indicates sensitivity of the device. Another important factor is response time which indicates how fast the device can react and recover. Time response of this device is tested under 3V bias under on/off switch of $20\mu W/cm^2$ UV illumination, which is marked with caption in Fig.6 (a). As shown in the figure, current instantly increases when UV is switched on and instantly recovers to initial state when UV is switched off. The rise and recovery edges are magnified and shown in Fig.6 (b) and (c). Rise time is defined as the time to reach 90% of the stable photocurrent, and the decay time is the time to reach 1/e (37%) of the original photocurrent. From the magnified edges, rise and decay time are estimated to be 0.7s and 0.5s respectively. Such a fast response should be attributed to the high charge separation ability by Graphene. In conventional configurations, a bias voltage is applied to build electric field in the material in order to rapidly separate charge carriers. In our hybrid material, this separation process is further accelerated by Graphene due to its superb ability to capture electrons.

On the other hand, the photodetector current can fully recover to initial state after removing the UV illumination. For realistic applications, if the photodetector cannot return to initial state after cycles, its precision and repeatability cannot be assured which means failure of the device. After UV illumination is switched off, the dark current of the device remains the same as that before UV illumination, which indicates that the device can fully recover and work

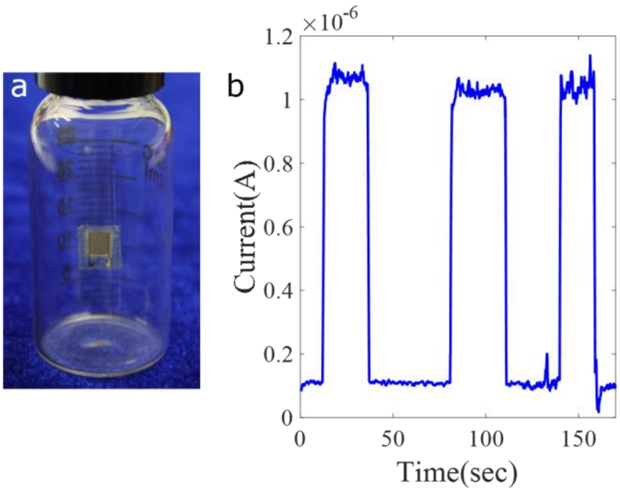

Figure 7: (a) Photo of a flexible photodetector based on TiO_2/Graphene hybrid attached on a glass bottle; (b) Time response of this photodetector under on/off switch of $20\mu W/cm^2$ UV illumination at 3V bias.

through cycles with low deviation.

Moreover, the photodetector is fabricated on flexible Parylene-C substrate and the material can tolerate bending because of the flexibility of Graphene which can support the TiO_2 nanoparticles when the device is bent. The device is attached on a bottle and bent to a radius of ~5cm to test its flexibility, as demonstrated in Fig.7. Though the photocurrent value has a 25% decline compared with that under unbent condition, the photodetector still reveals good repeatability and fast response in the flexibility test. The photocurrent decline may be ascribed to the material deformation while the device is bent. But since Graphene sheet is flexible, the hybrid material structure is not destroyed and can restore its morphology after returning to unbent state.

CONCLUSIONS

In summary, a novel ultraviolet (UV) photodetector based on TiO_2/Graphene hybrid has been demonstrated. The Graphene sheets help to support the TiO_2 nanoparticles and collect the photo generated electrons with high efficiency. The large surface area and restrain of electron-hole recombination brought by Graphene enhance the performance of TiO_2/Graphene hybrid which leads to great responsivity (0.304A/W) and sub second level response with rise time and recovery time of 0.7s and 0.5s, respectively.

The whole device is fabricated on flexible Parylene-C substrate, and the hybrid material exhibits high flexibility because the Graphene sheets which load the TiO_2 nanoparticles are resilient. Hence the flexibility test in which the device is attached on a bottle with bending radius of ~5cm still reveals acceptable performance and repeatability. Furthermore, this work is potential for developing photodetectors for wearable electronics.

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REFERENCES

[1] L.W. Sang et al., "A Comprehensive Review of Semiconductor Ultraviolet Photodetectors: From Thin Film to One-Dimensional Nanostructures", Sensors, 13, 10482-10518, 2013.

[2] Z.C. Liu et al., "Fabrication of UV Photodetector on TiO_2/Diamond Film", Nature Scientific Reports, 5, 14420, 2015.

[3] A. Fujishima et al., "Electrochemical Photolysis of Water at a Semiconductor Electrode", Nature, 238, 37-38, 1972.

[4] K. Hashimoto et al., "TiO_2 Photocatalysis: A Historical Overview and Future Prospects", Japanese Journal of Applied Physics, Vol.44, 8269-8285, 2005.

[5] J. Xing et al., "Highly sensitive fast-response UV photodetectors based on epitaxial TiO_2 films", J. Phys. D: Appl. Phys., 44, 375104 (5pp), 2011.

[6] H.G. Yang et al., "Solvothermal Synthesis and Photoreactivity of Anatase TiO_2 Nanosheets with Dominant {001} Facets", J. Am. Chem. Soc., 131, 4078–4083, 2009.

[7] N. Venkatachalam et al., "Sol–gel preparation and characterization of nanosize TiO_2: Its photocatalytic performance", Materials Chemistry and Physics, 104, 454–459, 2007.

[8] J. Zou et al., "Ultraviolet Photodetectors Based on Anodic TiO_2 Nanotube Arrays", J. Phys. Chem. C, 114, 10725–10729, 2010.

[9] T.D. Tao et al., "Chemically synthesized nanowire TiO_2/ZnO core-shell p-n junction array for high sensitivity ultraviolet photodetector", Appl. Phys. Lett. 103, 193119, 2013.

[10] X.D. Dong and et al., "High Performance Photo Electrochemical Type Self-Powered Ultraviolet Photodetector Using Epitaxial TiO_2/SnO_2 Branched Heterojunction Nanostructure", Small, 9, No.11, 2005-2011, 2013.

[11] Y. Xie et al., "A self-powered UV photodetector based on TiO_2 nanorod arrays", Nanoscale Research Letters, 8, 188, 2013.

[12] F. Guo et al., "A nanocomposite ultraviolet photodetector based on interfacial trap-controlled charge injection", Nature Nanotechnology, Vol 7, 798-802, 2012.

[13] H. Xia et al., "Organohalide lead perovskite based photodetectors with much enhanced performance", Chem. Commun., 50, 13695, 2014.

[14] S. Pei et al., "Direct reduction of graphene oxide films into highly conductive and flexible graphene films by hydrohalic acids", Carbon, 48, 4466–4474, 2010.

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