

Article

Effect of Ag/rGO on the Optical Properties of Plasmon-Modified SnO₂ Composite and Its Application in Self-Powered UV Photodetector

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Abstract: A facile hydrothermal method was employed to synthesize silver-reduced graphene oxide (Ag/rGO) plasmon-modified SnO₂ composite, by incorporating Ag-reduced graphene oxide (Ag/rGO) into SnO₂ nanorods as a photoanode for assembling a self-powered ultraviolet photodetector (UVPD). The as-synthesized samples were investigated in detail by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, and UV visible spectrophotometer. The as-prepared Ag/rGO films show enhanced light absorption attributed to the localized surface plasmon resonance (LSPR). The optimized 1.0 wt.% Ag/rGO incorporated into SnO₂-based UVPD exhibits a significant photocurrent response due to the enhanced absorption light and effective suppression of charge recombination. This UVPD demonstrates a high performance, with photocurrent density reaching 0.29 mAcm⁻² compared to the SnO₂-based device with 0.16 mAcm⁻². This device also exhibits a high on:off ratio of 195 and fast response time, which are superior to that of the free-modified one. In addition, the UVPD based on plasmon-modified SnO₂ photoanode treated with TiCl₄-aqueous solution has attained a higher photocurrent with a maximum value reaching 5.4 mAcm⁻², making this device favorable in ultraviolet detection.

Keywords: UV photodetector; surface plasmon; Ag/rGO; SnO₂ nanorod; plasmon-modified-SnO₂ composite

1. Introduction

Owing to the arising demand for precise detection of ultraviolet radiation in civil and military applications, the development of ultraviolet photodetectors with energy efficiency, a sustainable optical energy detection system, and essential and cost-effective wide bandgap material, such as TiO₂, SnO₂, ZnO, GaN, SiC, graphene, MoS, and quantum dots, have become vital [1–8]. In addition, the development of modern ultraviolet photodetectors is necessary, because the human body is sensitive to UV radiation that may cause different diseases, including cataracts and skin cancer [9–12]. Hence, self-powered photoelectrochemical (PEC)-type UV photodetectors (UVPDs) have emerged as a promising optoelectronic device based on photovoltaic effect, that meet the demand of energy efficiency, simple fabrication process, small size, reduced weight, cost-effective, and outstanding photodetection performance for a next generation nanodevice [10,13–15].

Among the various nanostructured materials [16–18], tin oxide (SnO₂) has emerged as one of the most potential wide bandgap materials owing to its outstanding properties, such as excellent optical sensitivity [19], larger bandgap (3.6–3.8 eV) [20], and higher electronic mobility (~100–200 cm²V⁻¹s⁻¹). A lot of progress has been made in fabricating SnO₂-based photoanodes for UVPDs and dye-sensitized

solar cells (DSCs) [21–25]. However, the SnO₂-based UVPDs so far have been reported as demonstrating significantly low photocurrent and poor photoresponse, due to their ~300 mV positive shift in the conductive band edge of SnO₂ and lower trapping density with numerous recombination sites, which limit their application in optoelectronics devices [26]. However, several techniques such as shape and particle size control [27–30], metal deposition [31–33], and hybridized carbon material [34,35] have been employed to prepare SnO₂-based photoanode materials. The photonic and optoelectronic devices made up of plasmon silver and graphene are gaining considerable attention as an effective approach to boost the efficiency of these devices [36–38].

Recently, Ag nanoparticles and graphene hybrid composites have emerged as promising modifying plasmonic materials to improve the performance of UV photodetectors via Ag-reduced graphene oxide plasmon composite [39–42]. Graphene hybrid composites have been well-known as suitable material due to the intrinsic favorable properties of graphene and its ability to store or transport charged electrons [43,44]. Significant development has been reported regarding the synthesis and application of Ag/rGO [45]. Hence, Keshvari et al. [46] reported a triboelectric nanogenerator that works as an active self-powered UV detector with enhanced contact surface area owing to the plasmon-assisted photoresponse in reduced graphene-Ag nanoparticles heterostructure. Paria et al. [10] synthesized graphene sheets decorated by silver nanoparticles, forming plasmonic graphene–Silver hybrid composites for a sensitive photodetector, demonstrating a 3.2 AW^{−1} plasmon photoresponse enhancement in the wavelength range from 330 to 450 nm. Owing to the unique and excellent properties of graphene, it could be employed to stabilize silver nanoparticles as active photonic material for improving the efficiency of plasmonic UV photodetectors [47]. However, the incorporation of Ag/rGO plasmonic hybrid composites into SnO₂ nanorods for self-powered UV photodetectors, to the best of our knowledge, has not much been investigated.

Herein, a silver nanoparticles and reduced graphene oxide (Ag/rGO) composite incorporated into SnO₂ NRs were utilized as photoanodes for PEC-type self-powered UVPDs. The Ag/rGO plasmonic hybrid composite was synthesized by solvothermal method and simultaneously reduced without using any hazardous reducing agent. In order to gain the detailed morphological, structural, and optical information, the as-synthesized plasmon-modified SnO₂ composite and SnO₂ nanorods were characterized with X-ray diffraction, scanning electron microscope, Raman spectra, and UV-Visible absorption spectroscopy. The plasmonic effect of Ag/rGO hybrid composites on the performance of plasmon-modified SnO₂-based PEC-type UVPD is also investigated. To evaluate the performance of PEC-type self-powered UVPDs, the on:off ratio, response time, and the photocurrent vs. light intensity were measured.

2. Experimentals

2.1. Materials

All chemicals were purchased and used without further purification, unless otherwise stated. Tin (IV) chloride pentahydrate (SnCl₄·5H₂O, 99%, Aladdin, Shanghai, China), graphite flakes (Sigma-Aldrich, Cat # 33246, ~ 150 μm flakes, Shanghai, China), potassium permanganate (KMnO₄ 99%) concentrated sulfuric acid (H₂SO₄ 95–98%), ethanol (anhydrous, 99.5%), sodium hydroxide (NaOH, 97%), and ethylene glycol were purchased from Aladdin (Shanghai, China), chloroplatinic acid hexahydrate (37.5%) and isopropyl alcohol (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) 1,3-dimethylimidazolium (DMIL, 98%), lithium iodide (LiI, 99%), iodine (I₂, 99%), tert-butylpyridine (TBP, 96%), guanidinium thiocyanate (GNCS, 99%), acetonitrile (99.8%), valeronitrile (99.5%), tert-butanol (99%), ethyl cellulose powders (Nos. 46070 and 46080), α-terpineol (96%), and chenodeoxycholic acid (98%) were purchased from Aladdin (Shanghai, China).

2.2. Synthesis of Graphene Oxide

Graphene oxide was prepared from natural graphite by a modified Hummer's method [48]. Typically, 1 g of graphite flakes, 0.5 g NaNO_3 , and H_2SO_4 were mixed, stirring in an ice bath for 1 h. Then, 3 g of KMnO_4 was slowly added into the mixture till the solution turned green. The solution was transferred to water bath at 35 °C and stirred for 1 h. Hence, 40 mL of deionized water was added to the thick solution and stirred for 1 h at a temperature of 90 °C. A total of 12 mL of H_2O_2 was slowly added and the color changed from dark brown to yellow. The resultant solid was removed by filtration, washing with 10% HCl and deionized water several times. The graphite oxide was dried at 50 °C till dried. A total of 100 mg of the dried graphite oxide was dispersed into 100 mL deionized water under ultrasonic for 30 min. A uniform brown graphene oxide (GO) solution (1 mg/mL) was formed.

2.3. Synthesis of Ag/rGO Hybrid Composite

Briefly, the Ag-graphene hybrid composite was synthesized as follows [49]: A uniform aqueous solution of graphene oxide (GO) was obtained when 50 mg of GO was dispersed in deionized water and sonicated for about 3 h, reaching a concentration up to 1 mg/mL. A total of 100–300 mg of silver nitrate (AgNO_3) was dissolved into 10 mL of deionized water and transferred to 30 mL ethylene glycol. After stirring for 30 min, the aliquot of GO suspension was added into the silver solution and stirred. Then, 0.34 g sodium citrate was slowly added into the solution as a reducing agent, and the suspension was transferred to hydrothermal oven and heated to 110 °C for 2 h. The as-prepared product was filtered, washed with deionized water, and finally dried in vacuum oven.

2.4. Fabrication of SnO_2 Nanorods and Incorporation of Ag/rGO into SnO_2 Nanorods

Briefly, SnO_2 NRs were synthesized by hydrothermal method [50]. Typically, 10 mL of aqueous sodium hydroxide were slowly added drop by drop to 40 mL of equal deionized water–ethanol containing 2.8 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. After stirring for 30 min, the mixed solution was transferred to a Teflon-lined stainless steel autoclave and kept in hydrothermal oven for 24 h. The obtained precipitates were centrifuged, washed with deionized water and ethanol several times, and finally dried in vacuum oven at 60 °C. A known content of Ag/rGO was dissolved into 40 mL ethanol and transferred into homogenous dispersion of 1.0 g of SnO_2 nanorods in 40 mL ethanol under vigorous stirring and sonication. The resultant solution was transferred to the stainless steel autoclave and treated at 120 °C for 24 h. After cooling to room temperature, the precipitate was centrifuged, washed, and dried to powder in vacuum oven at 80 °C overnight.

2.5. Device Fabrication

The SnO_2 and Ag/rGO- SnO_2 paste were prepared according to the standard procedures described somewhere else for DSCs [51]. Initially, the F-doped SnO_2 glass (FTO Nippon sheet glass, Japan $15 \Omega\text{cm}^{-1}$, 2.2 mm thick) were thoroughly washed by a detergent, deionized water, and ethanol in an ultra sonicator for 20 min each step. The SnO_2 and Ag/rGO- SnO_2 pastes were screen-printed on the F-doped SnO_2 glass electrodes via a doctor blade technique followed by sintering at 500 °C for 30 min. The photoanodes were dipped into TiCl_4 solution for 30 min at 70 °C and sintered again at 450 °C after 45 min in air, and maintained at 450 °C at a heating rate of 5 °C/min for 30 min. The PEC-type UVPDs were assembled according to the procedures similar to that reported by DSCs shown in Figure 1. Ag/rGO- SnO_2 screen-printed film was employed as a photoanode with an area of $\sim 0.28 \text{ cm}^2$ and thickness of $\sim 7.5 \mu\text{m}$. The platinum (Pt) catalyst was coated onto cleaned FTO glass by a brush painting method as counter electrodes. The photoanode and counter electrode were assembled into a sealed sandwich arrangement with internal spacers separating them. The iodine-iodide (I^-/I_3^-) electrolyte was introduced into the structure by vacuum-filling method and the hole was sealed with glass cover.

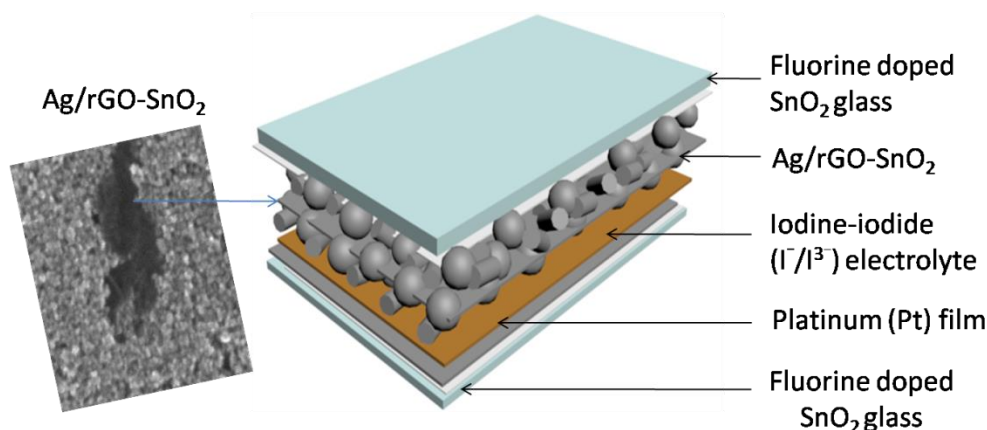


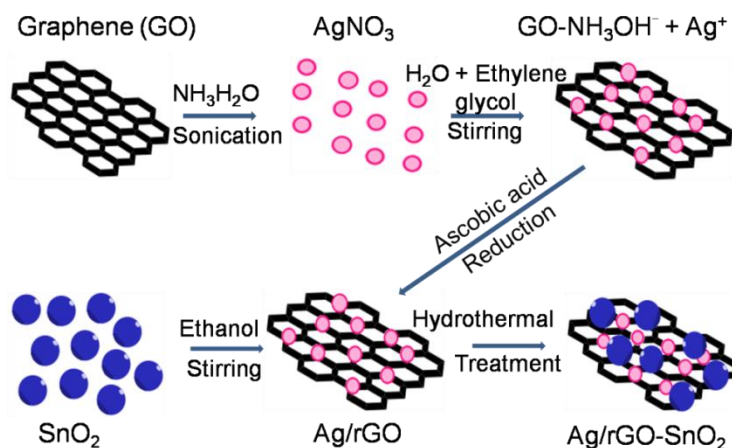
Figure 1. The structure of Ag/reduced graphene oxide-SnO₂ based photoelectrochemical self-powered ultraviolet photodetector.

2.6. Characterization

The morphology and structure of as-prepared samples were characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD, PANalytical, X pert PRO, with Cu, K α radiation, $\lambda = 1.5418 \text{ \AA}$), and Raman spectroscopy system (LabRam, HR800, Jobin Yvon, Longjumeau, France). Absorption characteristics were examined by UV-Vis spectrophotometry. The photocurrent–voltage characteristics were investigated using a Keithley 2400 SMU instrument and recorded using the custom Lab View virtual instrument program. The photoresponse switching behavior experiment was recorded using illumination of UV LED (NCSU033B, (T), Nichia) at a wavelength of 365 nm, as the source of light, with an electrochemical workstation (Autolab, PGSTAT302N).

3. Results and Discussion

The synthesis mechanism for the formation of the Ag/rGO hybrid composite and plasmon-modified SnO₂ composite is illustrated in Scheme 1. Firstly, ammonia solution was mixed with graphene (GO) and reacted with GO functional group to form a negative charge on the surface of GO [52]. After AgNO₃ was added, the negatively-charged GO was combined with the positively-charged Ag⁺ ions to form a complex of Ag⁺-GO-NH₃OH[−] ions. Consequently, the ascorbic acid was added into the solution and heated at 110 °C for 2 h to induce reduction in both Ag⁺ and GO-NH₃OH[−] ions resulting into the formation of the Ag/rGO hybrid composite. Then, the Ag/rGO composite was incorporated into SnO₂ nanorods.



Scheme 1. Preparation of Ag/reduced graphene oxide (Ag/rGO) and plasmon-modified SnO₂ (Ag/rGO-SnO₂) composites.

The morphology of as-synthesized samples was examined by scanning electron microscopy (SEM). In Figure 2a, the SEM image shows that graphene (GO) sheets exhibit continuous wave-like sheets with flake-like shape and wrinkles on the surface, demonstrating their flexibility. Figure 2b shows the SEM image of Ag/reduced graphene oxide (Ag/rGO) in which Ag particles were embedded in the hybrid composite as well-dispersed minute particles, whereas graphene provides support and stability to Ag nanoparticles (NPs) from aggregation. Ag NPs act as zero-dimensional nanospacers to increase the interlayer spacing and to prevent the graphene sheets restacking. As shown in Figure 2c, the SnO₂ nanorods were uniformly distributed in morphology and particle size. The SEM image of Ag/rGO incorporated into SnO₂ (Ag/rGO-SnO₂) in Figure 2d shows that SnO₂ nanorods (NRs) were attached to the surface of Ag/rGO particles. The size of Ag NPs was reduced, which could be attributed to the incorporation of Ag/rGO into SnO₂.

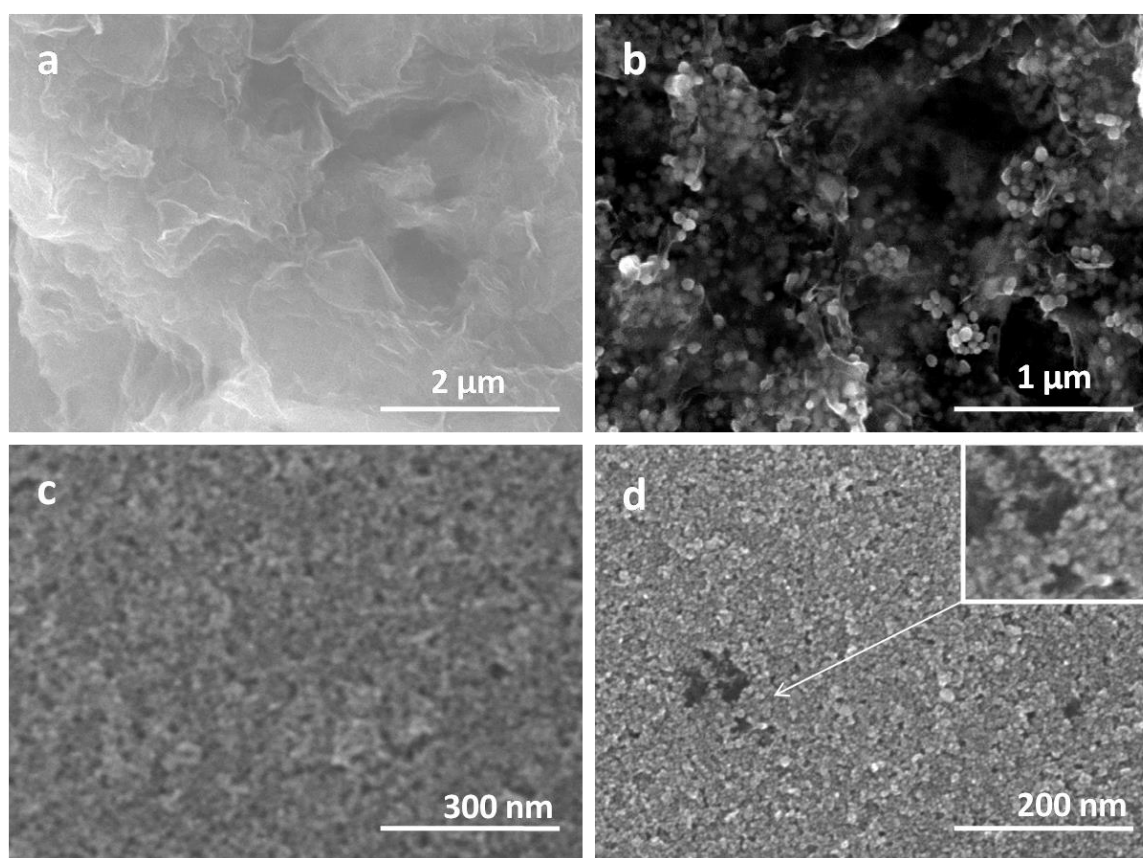


Figure 2. Morphological characterization: (a–d) top surface scanning electron microscopy (SEM) images of (a) graphene (GO), (b) Ag/reduced graphene oxide (Ag/rGO), (c) SnO₂ nanorods (NRs) and (d) 1.0 wt.% Ag/rGO incorporated into SnO₂ nanorods (1.0 wt.% Ag/rGO).

Structural properties of dried pristine graphite, graphene (GO), and Ag/reduced graphene oxide (Ag/rGO) composite are shown in Figure 3a. The typical X-ray diffraction (XRD) pattern of graphite displays a sharp peak located at around 26.38°, corresponding to an inter-layer spacing of 3.38 Å between 002 atomic planes. The diffraction peak of GO was shifted to around 11.6°, which correspond to the inter-layer spacing of 7.64 Å for 001 atomic plane. This inter-layer spacing value was much larger than that of graphite, which confirmed the oxidation of graphite. While the diffraction peaks for the as-synthesized Ag/rGO hybrid composite revealed intense peaks at $2\theta = 38.11^\circ$, 44.31° , 64.45° , and 77.41° , which were assigned to the (111), (200), (220), and (311) planes of Ag (JCPDS No. 065-8428), respectively, indicating the presence of Ag NPs in the face-centered cubic (fcc) phase.

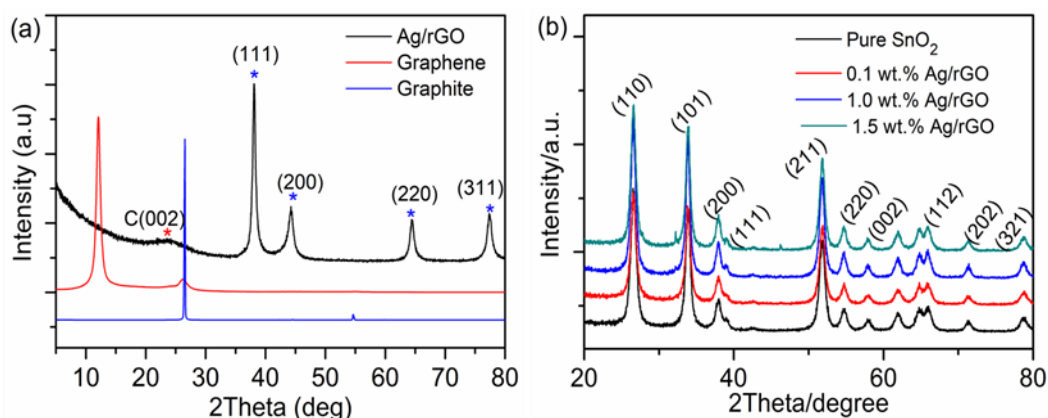


Figure 3. Diffraction (XRD) patterns of (a) graphite, graphene, and Ag/reduced graphene oxide (Ag/rGO) hybrid composite; (b) SnO₂ nanorods and 0.5 wt.% Ag/rGO, 1.0 wt.% Ag/rGO 1.5 wt.% Ag/rGO hybrid composite, respectively, incorporated into SnO₂ nanorods.

The sharp diffraction peak for GO was absent in Ag/rGO, but a weak and broad peak appears in the range 20°–30°, attributed to a high-degree exfoliation of the graphene sheet in Ag/rGO due to the introduction of Ag NPs. The inter-layer spacing value of Ag/rGO was less than that of GO, suggesting the reduction of GO [53]. This result demonstrates that Ag NPs could be successfully incorporated with GO. Figure 3b shows the powder X-ray diffraction patterns of SnO₂ nanorods and the incorporated optimized content of the Ag/rGO hybrid composite. It was observed that most diffraction peaks of SnO₂ nanorods were well indexed to tetragonal rutile tin oxide (JCPDF: 41–1445). No clear diffraction peaks associated with reduced graphene oxide (rGO) were identified in composite films, which might be due to the low amount of Ag/rGO added into SnO₂. The XRD analysis revealed that the lattice parameters (*a*, *b*, and *c*) of the tetragonal cell were achieved. The lattice parameters *a* and *b* of 1.0 wt.% Ag/rGO (*a* = *b* = 4.73 Å) became larger than that of SnO₂ (*a* = *b* = 4.72 Å), while the lattice parameter of *c* showed negligible change (*c* = 7.17 Å) for both 1.0 wt.% Ag/rGO and SnO₂. The enlargement of the unit cell could be due to the replacement of the smaller O^{2−} by larger Ag⁺ and GO[−] ions in the SnO₂ cells. In addition, the average grain size of the 1.0 wt.% Ag/rGO crystallite estimated from the (110) Bragg reflection was ca. 106.8 nm according to Scherer's equation, and the average grain size of the SnO₂ crystallite was ca. 88.8 nm.

The Raman spectra of GO and Ag/rGO with their characteristic peaks were displayed in Figure 4a. The Raman spectra of GO exhibits the D band and G band located near 1580 and 1354 cm^{−1}, respectively. It is noted that the intensity ratio of D and G for GO corresponds to 0.83, while the Raman spectra of the Ag/rGO hybrid composite consists of two peaks located at ~1354 and 1601 cm^{−1} corresponding to D and G bands of graphene with intensity ratio of 1.08. In contrast to GO, the response of Ag/rGO reveals sharp D and G peaks with an increase in D peak intensity relative to the G peak after reduction. The increased value of I_D/I_G for Ag/rGO conversely related to the broken hexagonal lattice structure and increased defects suggests a large disorder was induced when Ag NPs were assembled over graphene [54].

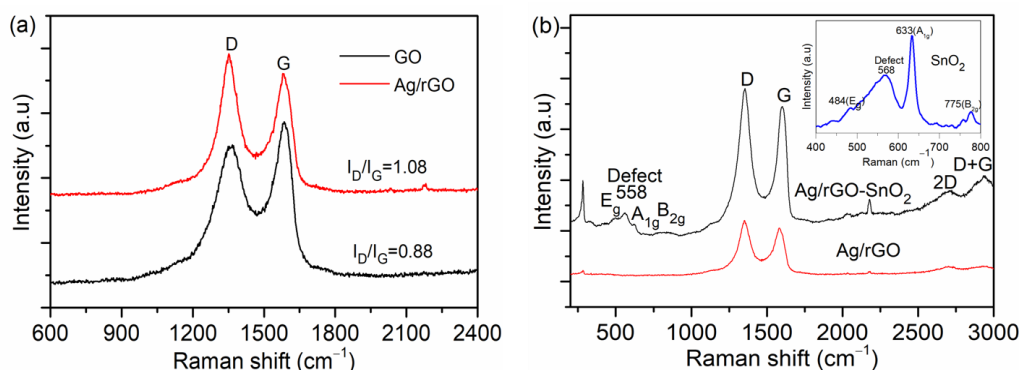


Figure 4. Raman spectra of (a) graphene (GO) and Ag/reduced graphene oxide (Ag/rGO) films; (b) Ag/rGO, SnO₂, and Ag/rGO incorporated into SnO₂ (Ag/rGO-SnO₂).

Hence, the main characteristic peaks of the Ag/rGO hybrid composite were significantly enhanced due to the strong plasmonic near field around silver nanoparticles. As shown in Figure 4b, the broad Raman spectrum of the Ag/rGO-SnO₂ film was observed at 1353 and 1596 cm^{-1} , corresponding to the relative intensity ratio value of 1.01. A slight red-shift was depicted at the lowest range of about 400–800 cm^{-1} related to SnO₂ films in Ag/rGO-SnO₂, which could be ascribed to the induced defects due to Ag/rGO loading [55]. Moreover, the G peak was down-shifted to 1596 cm^{-1} on Ag/rGO-SnO₂ film. This shift in G peak confirmed the occurrence of electron transfer between Ag/rGO and SnO₂ in the Ag/rGO-SnO₂ composite. This result suggests that electron transfer from Ag NPs to SnO₂ occurs through sp^2 carbon domains of graphene derivatives [56].

UV-Vis spectral analysis was conducted to examine the light absorption spectra of as-prepared samples. Figure 5a exhibits two important maxima related to GO at a peak near 238 nm, which corresponds to C–C bonds, and a shoulder at around 304 nm corresponds to transition of the C=O bond, which is attributed to the sp^3 bonding in graphene [57]. The strong broad peak observed at ~440 nm is a characteristic of the Ag/rGO composite observed after Ag NPs were encapsulated with graphene nanosheets and reduced by ascorbic acid (Figure 5a) [58]. The UV-Vis absorption of the Ag/rGO red-shift to 440 nm and generate broadening as a results of strong light scattering due to the large size of nanoparticles and the formation of network structure [59,60]. These experimental results suggest that absorbance of Ag/rGO could be spectrally tunable [61]. Figure 5b shows the UV-Vis spectra of SnO₂ and Ag/rGO-SnO₂. It could be seen that SnO₂ exhibited absorption mainly in the UV region within 200 to 300 nm. The Ag/rGO-SnO₂ showed the optical spectra in both the UV and the visible light region, which was significantly larger than that of SnO₂. Compared to SnO₂, the composite films exhibited a red-shift attributed to the optical vibration caused by surface plasmon resonance (SPR) of Ag. However, due to the low concentration of Ag and graphene, the increase of absorption of Ag/rGO-SnO₂ is not prominent as it is over shadowed by more prominent SnO₂ absorption [62–64]. Figure 6 illustrates the optical transmittance of SnO₂, Ag/rGO, and Ag/rGO-SnO₂. The transmittance of SnO₂ and Ag/rGO film rises to 84% and 74% corresponding to wavelengths at 550 and 326 nm, respectively. The drop in transmittance of Ag/rGO is attributed to the imperfection resulting from polymeric material and graphene wrinkling [65]. It is well known that Ag atoms have high UV light absorption around the 400 nm region. However, the encapsulation of Ag by graphene as a protective layer blocks the formation of surface plasmon light and decreases the light absorption [66]. Compared to SnO₂, the transmittance of Ag/rGO-SnO₂ film has decreased to around 80% due to the impact of the Ag/rGO composite.

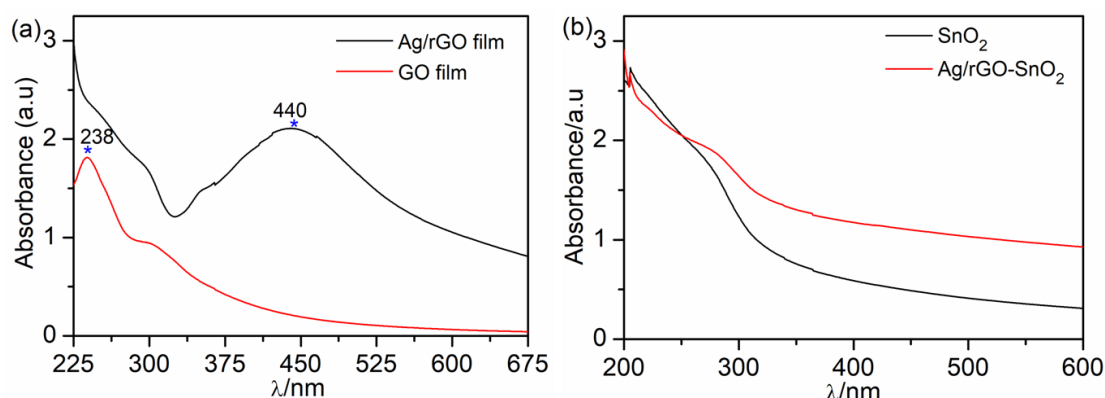


Figure 5. UV-Vis absorbance of (a) graphene (GO) and Ag/reduced graphene oxide (Ag/rGO) films; (b) SnO₂, Ag/rGO, and Ag/rGO incorporated into SnO₂ (Ag/rGO-SnO₂) composite.

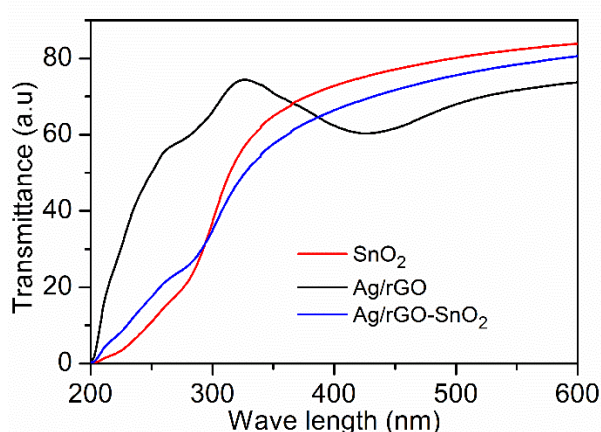


Figure 6. UV-Vis transmittance spectra for SnO₂, Ag/reduced graphene oxide (Ag/rGO) hybrid composite, and Ag/rGO incorporated into SnO₂ (Ag/rGO-SnO₂) composite.

The photocurrent (J)–voltage (V) characteristics for UVPDs with optimized Ag/rGO incorporated into SnO₂ as photoanodes, and compared to SnO₂ photoanode under UV illumination, is shown in Figure 7a. Compared to pure SnO₂ device, which shows a 0.14 mAcm^{-2} value, the J_{sc} of devices exhibited higher values when SnO₂ nanorods were incorporated. A maximum value of $J_{sc} = 0.29 \text{ mAcm}^{-2}$ was obtained for 1.0 wt.% Ag/rGO hybrid composites. This increment could be ascribed to the enhancement of light absorption and the effective suppression of charge recombination. In order to examine and evaluate the photocurrent response in detail, device dynamic performances were measured under UV light irradiation of 365 nm at zero bias with a power of 40 mWcm^{-2} . The illumination was periodically switched on/off at intervals of 10 seconds with incident light from solar simulator at zero bias. Figure 7b shows the photocurrent time response of these devices with different content of Ag/rGO incorporated into SnO₂ and compared to SnO₂ device. The repeatable cycles observed in photocurrent signals without decay demonstrates an outstanding reproducibility and stability for the UVPDs. The rise time and decay time of the photocurrent response was calculated from data of Figure 7b. The rise time (t_r) is often defined as the time taken by the photocurrent to increase from 0% to 63% (i.e., $1 - 1/e$) of the maximum value, and the decay time (t_d) is the time taken by the photocurrent to decrease from the maximum value to 37% (i.e., $1/e$) [13,67]. This device exhibited a rapid dynamic response for rise and decay time (as shown in Figure 7c). The τ_r and τ_d values for UVPDs with the 1.0 wt.% Ag/rGO photoanode were estimated to be 0.341 s and 0.068 s for the J , respectively. The τ_r and τ_d values for UVPD with the 1.5 wt.% Ag/rGO photoanode were estimated to be 0.164 s and 0.112 s, respectively, as shown in Figure S1.

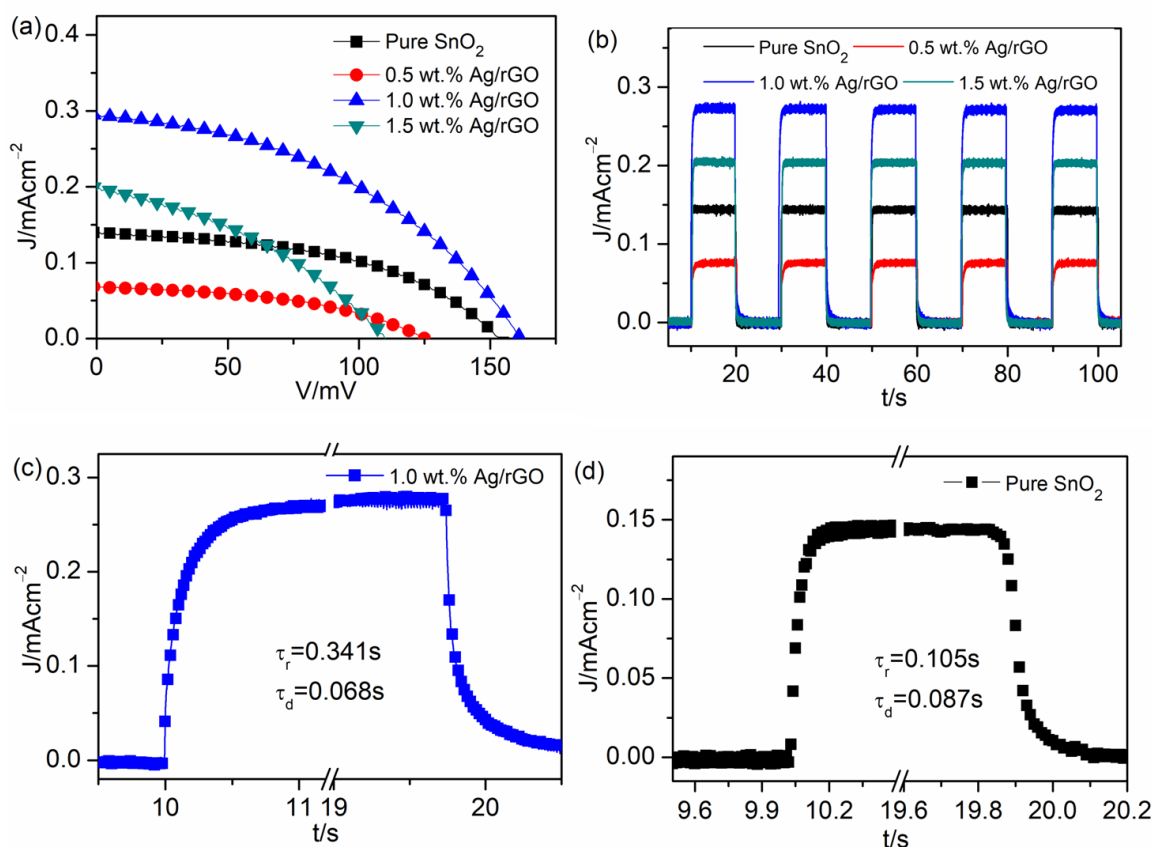


Figure 7. (a) Photocurrent density (J) – voltage (V) characteristics and (b) photocurrent responses of ultraviolet photodetectors (UVPDs) based on the pure SnO₂ photoanode and 0.5 wt.% Ag/rGO, 1.0 wt.% Ag/rGO, and 1.5 wt.% Ag/rGO hybrid composite incorporated into SnO₂ photoanodes under an irradiance of 40 mW cm⁻² UV light ($\lambda = 365$ nm). (c,d) Enlarged rising and decaying edges of the photocurrent response for the Ag/rGO-SnO₂ and SnO₂-based UVPDs.

The τ_r and τ_d values for UVPDs of the free-modified SnO₂ photoanode were 0.13 s and 0.087 s, respectively, as shown in Figure 7d. The rapid rise time and decay time for UVPD with 1.0 wt.% Ag/rGO were shorter than that of the free-modified SnO₂ photoanode device, which reveal that Ag/rGO can significantly enhance the sensitivity of UVPD. The Ag/rGO-incorporated SnO₂ photoanode-based UVPD demonstrated a higher photocurrent, higher on/off ratio, and faster rise and decay time compared to the free-modified SnO₂ photoanode, as summarized in Table 1. This device exhibited an on/off photocurrent contrast ratio (ratio between photocurrent and dark current) reaching the highest value of 195, compared to 66 for the free-modified SnO₂-based device, suggesting that the UV photodetector would be suitable for measurement of UV light.

Table 1. Detailed data of short-circuit photocurrent density (J_{sc}), On:Off ratio, rise time and decay time for ultraviolet photodetector based on pure SnO₂ and different contents of Ag/rGO incorporated into SnO₂.

UVPD	J_{sc} (mA cm ⁻²)	On:Off Ratio	Rise Time (s)	Decay Time (s)
Pure SnO ₂	0.14	66	0.13	0.087
0.5 wt.% Ag/rGO	0.07	41	0.421	0.104
1.0 wt.% Ag/rGO	0.29	195	0.341	0.068
1.5 wt.% Ag/rGO	0.27	135	0.164	0.112

In addition, the TiCl₄-modified SnO₂ and TiCl₄-treated Ag/rGO-modified SnO₂ photoanodes were employed to assemble UVPDs. As shown in Figure 8a, the photocurrent–voltage characteristics of

devices based on TiCl_4 -treated SnO_2 photoanodes exhibit a significant increase. In particular, the device modified with 1.0 wt.% Ag/rGO displays a J_{sc} of 5.4 mAcm^{-2} .

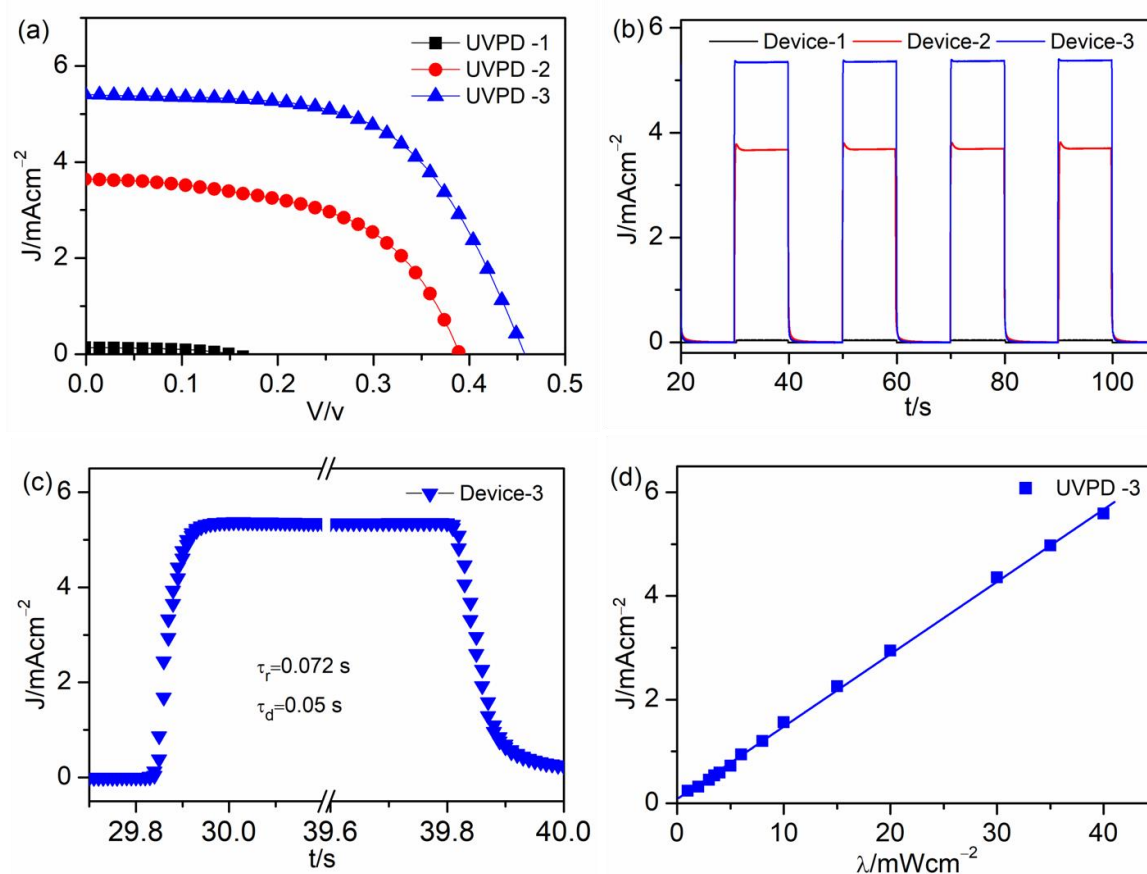


Figure 8. (a) J - V characteristics and (b) photocurrent responses of UVPDs based on the pure SnO_2 (UVPD-1), TiCl_4 -treated SnO_2 (UVPD-2), and 1.0 wt.% Ag/rGO (UVPD-3) under an irradiance of 40 mW cm^{-2} UV light ($\lambda = 365 \text{ nm}$). (c) Enlarged rising and decaying edges of the photocurrent response for the 1.0 wt.% Ag/rGO. (d) J as a function of the incident UV light intensity from 1 to 40 mW cm^{-2} .

This enhancement is attributed to the suppressed charge recombination. Figure 8b shows the photocurrent time response of these devices with 1.0 wt.% Ag/rGO incorporated into SnO_2 and compared to free-modified SnO_2 device. The τ_r and τ_d values for UVPDs with 1.0 wt.% Ag/rGO photoanode were estimated to be 0.341 and 0.068 s. These are the values reported for data of Figure 8c. This device exhibits an on/off photocurrent contrast ratio reaching the highest value of 2740, compared to 544.5 for the free-modified SnO_2 -based device. In summary, the UVPD assembled with the Ag/rGO-incorporated SnO_2 photoanode treated by TiCl_4 exhibits a higher photocurrent, higher on/off ratio, and faster rise and decay times compared to that of the free-modified SnO_2 photoanode, as summarized in Table 2. The increment in photocurrent is attributed to the presence of more photogenerated charge carriers produced by higher absorbed photon flux, proposing the UV photodetector be suitable for measurement of UV light. Figure 8d shows the photocurrent vs. the intensity of light for 1.0 wt.% Ag/rGO-based UVPD illuminated by UV light irradiation ($\lambda = 365 \text{ nm}$) with incident light power at zero bias. The J increased linearly as the light intensity increases from 1 to 40 mWcm^{-2} for the UVPD-3. This increment in photocurrent varied linearly with the increase in the intensity of UV light, proposing the UV photodetector may be best suited for measurement of UV light.

Table 2. Detailed data of short-circuit photocurrent density (J_{sc}), On:Off ratio, rise time and decay time for ultraviolet photodetector based on pure SnO₂ (UVPD-1), TiCl₄-treated SnO₂ (UVPD-2) and 1.0 wt.% Ag/rGO incorporated into SnO₂ (UVPD-3).

UVPDs	$J_{sc}(\text{mAcm}^{-2})$	On:Off Ratio	Rise Time (s)	Decay Time (s)
UVPD-1	0.14	66	0.13	0.087
UVPD-2	3.7	544	0.14	0.05
UVPD-3	5.4	1441	0.072	0.05

4. Conclusions

In summary, we successfully prepared Ag/rGO incorporated into SnO₂ nanorods by hydrothermal method. Ag/rGO-SnO₂-based PEC-type self-powered UV photodetectors were fabricated incorporating Ag/rGO into SnO₂ nanorods used as photoanodes. Compared to UVPDs based on pure SnO₂ photoanodes, the optimized UVPD with 1.0 wt.% Ag/rGO demonstrated a higher photocurrent benefiting from plasmon-enhanced UV-absorption and the effective suppression of the charge recombination at the contact interface. Moreover, this device showed a higher on:off photocurrent ratio of 195 and a rapid response speed (rise time 0.341 s and decay time 0.068 s). The self-powered PEC-type UVPD based on the TiCl₄-treated Ag/rGO-SnO₂ photoanode showed a high on:off ratio of 1441, a fast rise time and decay time ($\tau_r = 0.072$ s and $\tau_d = 0.05$ s), together with outstanding optical signal response and good reproducibility in a wide range of switching frequencies.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/9/12/648/s1>, Figure S1: the enlarged rising and decaying of edges of the photocurrent response ultraviolet photodetector based on SnO₂ incorporated with 1.5 wt.% Ag/rGO composite.

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