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ARTICLE

TiO₂ Enhanced Ultraviolet Detection Based on Graphene/Si Schottky Diode

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Graphene/Si has been proved to form quality Schottky junction with high photoelectric conversion efficiency at AM1.5. However, for the ultraviolet portion of the incident light, the photoelectric performance will degrade significantly due to severe absorption and recombination at the front surface. Herein, to realize enhanced ultraviolet detection with graphene/Si diode, TiO₂ nanoparticles (NPs, 3–5 nm) are synthesized and spin-coated on the graphene surface to improve the photoresponse in the ultraviolet region. According to our results, the conversion efficiency of the graphene/Si diode at 420 nm and 350 nm increases by 72.7% and 100% respectively with TiO₂ coating. Then C^2-V measurements of both TiO₂ and graphene/Si diode are performed to analyze the electronic band structure of the TiO₂/graphene/Si system, based on which we finally present the enhancement mechanism of photodetection by TiO₂ NPs.

Introduction

As a highly conductive and transparent material, graphene has been considered as a promising material in energy conversion.^{1–4} Solar cells and photodetectors based on graphene/Si Schottky heterojunctions have been widely reported in previous studies as two types of typical photovoltaic devices based on graphene.^{5–12} Such devices possess a very simple structure that graphene laying on the surface of n-type silicon substrate. In such structure, the Richardson constant of Si can be significantly lowered due to the finite density of states of graphene and thus results in a low leakage current, which has been proved using the Landauer transport model.¹³ Once the incident light arrives at the graphene/Si interface, carriers are excited and then separated by the built-in electric field to achieve the photoelectrical conversion process. Solar cell with such structure was firstly reported with initial power conversion efficiency (PCE) of around 1.5%.¹⁴ In the following five years, various approaches have been employed to improve its efficiency, including chemical doping,^{15–17} structural design,^{18–20} and electrolytes assistance²¹. In a recent work by our group, TiO₂ antireflection coating and acid doping were performed together to improve the PCE to 14.5% at AM 1.5, nearly decuple higher than the initially reported level.²²

The approaches applied above are quite valuable to enhance the photoresponse properties of graphene/Si based photodetectors. However, being different with a solar cell, the photodetector mainly focuses the response of light within a

certain wavelength range. The photoelectric conversion from different light wavelength can hardly be reflected by the investigation in solar cells. For example, ultraviolet will be strongly absorbed at the front surface of the device, resulting in severe recombination and thermal loss. Despite the PCE of the graphene/Si diode can be improved at AM 1.5, the ultraviolet response maybe still far lower than that in its optimal wavelength region. Thus it is meaningful to enhance the ultraviolet response of graphene/Si diode to widen its effective working spectrum range.

Introducing a functional layer for light absorption and conversion is a widely used method to improve the photovoltaic devices,^{23–28} and it is especially suitable to enhance the photoresponse and PCE of ultraviolet for graphene/Si diode according to the analysis above. TiO₂ is a common photocatalytic material with strong absorbance in the ultraviolet range.^{29–32} When irradiated by ultraviolet, excitons generated in TiO₂ may be used to enhance the response of graphene/Si diode via carriers injection. This is quite different from the case of long-wave light which is mainly based on the optical antireflection of TiO₂. In this work, the ultraviolet detection of graphene/Si diode was greatly improved by simply spin-coating a layer of TiO₂ nanoparticles (NPs) on the surface of device. The performances of the device before and after TiO₂ coating, including the current density-voltage ($J-V$) characteristics, responsivity, quantum efficiency, *etc.*, were compared to show the effects of the TiO₂ layer. The band diagram of the

TiO₂/graphene/Si system was then deduced from the $C^{-2}-V$ characteristics and finally a possible enhancement mechanism of the TiO₂ layer was presented.

Experimental

Synthesis of TiO₂ NPs

TiO₂ was synthesized by a nonhydrolytic sol-gel approach described as follows: After stirring a solution of TiCl₄ (1 mL), ethanol (5 mL), and benzyl alcohol (35 mL) for 6 h at 80°C, it was washed with diethyl ether for three times. The white TiO₂ precipitate was obtained by centrifuging the crude product. The final TiO₂ solution was prepared by dispersing it in ethanol.

Preparation of graphene

Multilayer graphene (MLG) was prepared by an atmospheric chemical vapor deposition method. Copper foil (25 μm, 99.8%, purchased from Alfa Aesar Chemical Co. Ltd.) was put in a tube furnace to be used as the substrate. Under the protection of Ar (200 mL/min) and H₂ (30 mL/min), the furnace was heated to 1000 °C in 50 min and further maintained for 30 min. Methane flow (20 mL/min) was then fed in as the carbon source. After 15 min reaction, the copper substrate was quickly moved away from the heating zone and cooled down to room temperature. The copper substrate was then removed in 0.5M FeCl₃ and graphene was successively transferred to deionization water and rinsed thoroughly to clean the residual FeCl₃ and other impurities.

Fabrication of the device

MLG was directly transferred on an n-type silicon substrate with SiO₂ layer along its surface borders (window area is ~0.1 cm²). After drying in air, TiO₂ NPs dispersed in ethanol (0.2 mg/mL) was spin-coated on the surface of graphene at 2000 r/min for 30 s, as illustrated in Figure 1a. Silver paste and deposited Ti/Au layer were used as the top electrode and back electrode of the device, respectively. A typical photograph of the device (without electrodes) is shown in Figure 1b.

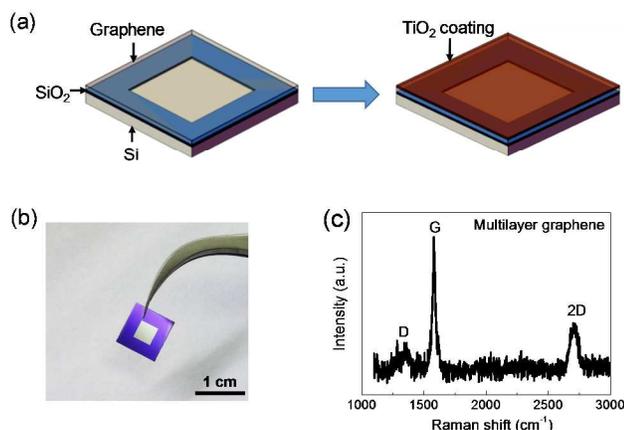


Figure 1. (a) Schematic of the device fabrication. (b) Photograph of the device. (c) Raman spectrum of the multilayer graphene. $I_{2D}/I_G \approx 0.34$.

$C^{-2}-V$ measurement

$C^{-2}-V$ measurement for TiO₂ NPs was performed by a Potentiostat (CHI 660D) using a three-electrode system. The Ag/AgCl and platinum electrodes were served as the reference and counter electrodes, respectively. TiO₂ NPs were spin-coated on an FTO coated glass to fabricate the working electrode. H₂SO₄ aqueous solution (0.5 M) was used as the electrolyte. The applied AC potential was 1 kHz with an amplitude of 0.01 V. Electrode potentials were converted to NHE using the relationship $V_{\text{NHE}} = V_{\text{Ag/AgCl}} + 0.197$ V. For the MLG/Si diode, the reference and counter electrodes were both connected with the top electrode of the device, and the work electrode connected with its back electrode. The frequency and amplitude of the applied AC voltage is 5 kHz and 0.01 V, respectively.

Characterizations

Raman spectra were collected by HORIBA LabRAM HR Evolution with 514 nm laser source. Scanning Electron Microscope (SEM) was performed by Zeiss Merlin compact. Transmission Electron Microscope (TEM) was performed by JEM-2010 TEM. UV-Vis spectrum of graphene was measured by Agilent Cary 5000. Atom Force Microscope (AFM) was tested by Agilent N9451A. The thickness of the TiO₂ layer was measured by the KLA Tencor Surface Profilometry. The $J-V$ and on/off characteristics were recorded by Keithley 2601. X-ray photoelectron spectrum (XPS) was collected by XPS 250XI.

Results and discussion

In order to enhance the ultraviolet response of MLG/Si diode, TiO₂ layer was coated on the surface of graphene to utilize the light energy irradiated on the device more efficiently. In the TiO₂/MLG/Si sandwich system, graphene functioned not only as the functional layer to form Schottky junctions with both the Si substrate and TiO₂ layer, but also acted as the conductive layer through which the carriers transport to the external circuit. Figure S1 shows that the transmittance of the MLG was about 86.9% (at 550 nm). According to the 2.3% linear optical absorption of monolayer graphene to white light,³³ it could be deduced that as-synthesized MLG was about 6-layered, which was consistent with its Raman spectrum ($I_{2D}/I_G \approx 0.34$, Figure 1c).^{34,35} The metallic impurities in graphene may influence the diode behavior of MLG/Si device significantly.¹³ XPS study was performed to investigate the metallic impurities in as-prepared graphene samples. The result (Figure S2) shows quite low atomic percentage of Fe and Cu, the most possible metallic impurities introduced in graphene during preparing and transfer processes.

The morphology of TiO₂ NPs has a great influence on their improvement effects. Poorly-dispersed particles and thick bulk agglomeration will severely affect the carriers diffusion and separation, as well as reduce the light energy arriving at the MLG/Si interface. TEM image (Figure 2a) reveals that the TiO₂

NPs were well-dispersed with an average size of 3~5 nm. High resolution TEM (HRTEM) image further shows the lattice fringes of TiO₂ NPs. The inter-planar distance of 0.24 nm and 0.35 nm are corresponding to the (004) and (101) planes of anatase TiO₂. After being coated on MLG, SEM image (Figure 2b) shows that the TiO₂ NPs were uniformly spread on the MLG surface without obviously inconspicuous region such as cracks or holes.

AFM was further performed to characterize the morphology of the TiO₂ layer, as shown in Figure 2c. It can be observed that the TiO₂ NPs are self-assembled to be spherical agglomerations with larger sizes. Even so, the distribution of the agglomerated TiO₂ NPs still maintain uniform in general. The thickness of the TiO₂ layer was measured by Surface Profilometry, and the result (Figure 2d) showed that the average thickness of the TiO₂ layer was about 100 nm.

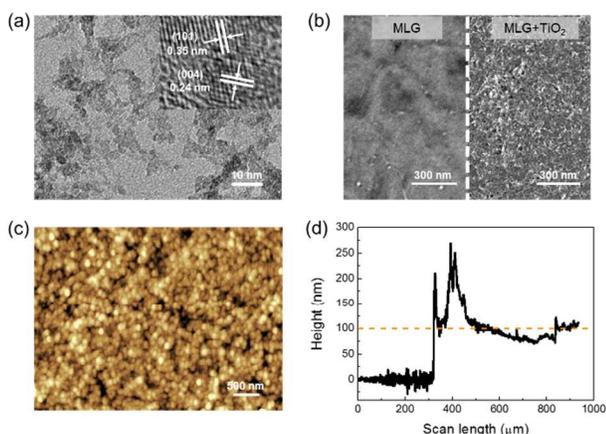


Figure 2. (a) TEM image of TiO₂ NPs. The mean size of TiO₂ NPs is about 3~5 nm. The inset shows a typical HRTEM image of TiO₂ NPs. (b) SEM images of MLG before (left) and after (right) TiO₂ coating. (c) AFM image of the TiO₂ layer. (d) Height changes from MLG to the TiO₂ layer. The thickness of the TiO₂ layer is about 100 nm.

The $J-V$ relationship is the most important and widely used characteristic for diode performance. $J-V$ characteristics of the devices were measured under a beam of 420 nm incident light with the intensity of 0.16 W/cm² (Figure 3a). It can be deduced that the initial photoelectrical conversion efficiency of the device is only 0.44%. After coated with TiO₂ NPs, the PCE increased to 0.76%, nearly 1.7 times higher than that of the original value. The open circuit voltage (V_{oc}) of the device was nearly stable, but the short circuit current density (J_{sc}) increased apparently, which contributed much to the increase of PCE. Acid doping has been reported to be another efficient way to improve the PCE of MLG/Si device.^{7,9} The TiO₂ coated device was then exposed to HNO₃ (analytical reagent) vapor for about 30 s. The blue curve in Figure 3a shows that the acid doping still worked efficiently to improve the PCE after being coated with TiO₂ NPs. The probable reason was that the HNO₃ vapor could permeate through the channels formed between TiO₂ NPs agglomerations to arrive the surface of graphene and then caused the doping effects. Being different from the only TiO₂

NPs coating, it can be seen from Figure 3a that the increase of V_{oc} and fill factor (FF) contributed the most part of the PCE improvement in the case of acid doping. This indicated that the enhancement mechanism of TiO₂ NPs was different from the doping effect of HNO₃. The obvious increase of J_{sc} after TiO₂ coating was probably because that the TiO₂ NPs could provide extra excited carriers when ultraviolet irradiated on the surface. This was also consistent with the band gap of TiO₂ (about 3.0~3.2 eV, corresponding to the wavelength of 388~413 nm).^{36,37} The band gap of nanoparticles was relevant to their sizes and crystal structures.^{38,39} The actual excited wavelength limit might fall in a wider range around 413 nm. As an example for the light with higher energy, $J-V$ characteristics of the device at 350 nm incident light (2.21 W/cm²) were also tested (Figure S3). The PCE of the device increased by 100% (from 0.065% to 0.13%) after TiO₂ coating, higher than the case at 420 nm. The dark $J-V$ characteristics (Figure 3b) show that neither TiO₂ coating nor acid doping would significantly affect the rectification behavior of the MLG/Si diode.

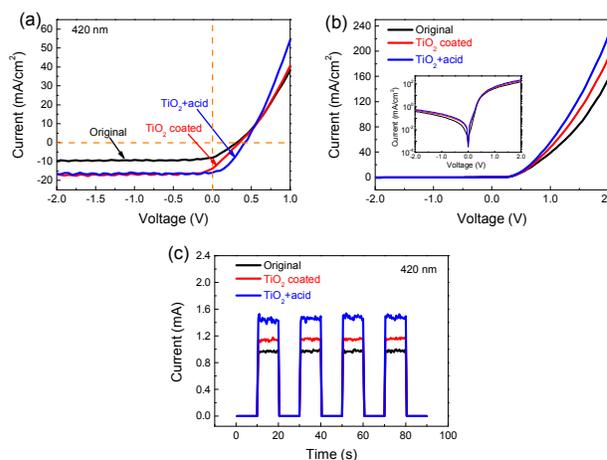


Figure 3. (a) Light and (b) Dark current-voltage characteristics of the device. The inset shows corresponding log-linear plots. (c) On/off characteristics of the device tested at 420 nm incident light.

Response current is another important parameter for a photodetector because it is usually used directly as the response or output signal of the device. On/off characteristics measurements were performed and the result is shown in Figure 3c. Thanks to the improvement of PCE, the response current (I_{resp}) at 420 nm increased from 0.97 to 1.15 mA, and finally reached 1.47 mA after acid doping. The TiO₂ coated device shows excellent repeatability of switching behavior (Figure S4) in 10 min. The response and recovery time are measured to be 1.30 ms and 2.76 ms, respectively (Figure S5), which are comparable to the values of graphene/Si photodetectors reported before.⁵ In addition, the thickness effect of TiO₂ layer on device performance has been discussed in Figure S6. The performance tested at different conditions are summarized in Table 1 to clearly show the improvements and differences.

To investigate the behavior of TiO₂ layer in a wider spectrum range, quantum efficiency was measured from 300 to

1100 nm. The results (Figure 4) show that the quantum efficiency in the near-ultraviolet range was obviously improved after TiO₂ coating.

Table 1. Photoelectric performance of the MLG/Si diode tested at 420 nm (0.16 W/cm²).

Structure	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE _{UV} (%)	I_{resp} (mA)	Responsivity (mA/W)
Original	300	7.11	32.78	0.44	0.97	60.6
TiO ₂ coated	300	12.02	33.87	0.76	1.15	71.9
TiO ₂ +acid	400	15.12	40.25	1.52	1.47	91.9

In order to illustrate more clearly, the relative change of quantum efficiency (ΔEQE) was calculated by $(EQE_{TiO_2 \text{ coated}} - EQE_{original}) / EQE_{original}$ and is shown as the blue curve in Figure 4, which can be separated into three typical areas (area I~III) along the decrease of the light wavelength. In area I, from 1100 nm to point A (570 nm), ΔEQE increased mildly from 0.01 to 0.12. The photon energy of the light in this area was too low to excite the electrons in TiO₂, so that the enhancement mechanism was mainly possible to be optical antireflection. In area II, from point A to point B (410 nm), ΔEQE turned to increase more quickly, indicating that parts of the TiO₂ NPs could be excited by the incident light to generate carriers, which contributed to the increase of ΔEQE . When the photons energy further increased (wavelength < point B), the carriers could be excited abundantly in TiO₂ layer, resulting in a sharp increase of the ΔEQE . It is worth to mention that light with too short wavelength may loss most of their energy in the TiO₂ layer and seldom photons can arrive at the MLG/Si interface, thus a peak value of ΔEQE may exist in area III. According to the analysis above, the quantum efficiency of the device in the whole range from 300 to 1100 nm can be improved continuously by TiO₂ coating based on both optical antireflection and carriers injection from TiO₂ layer.

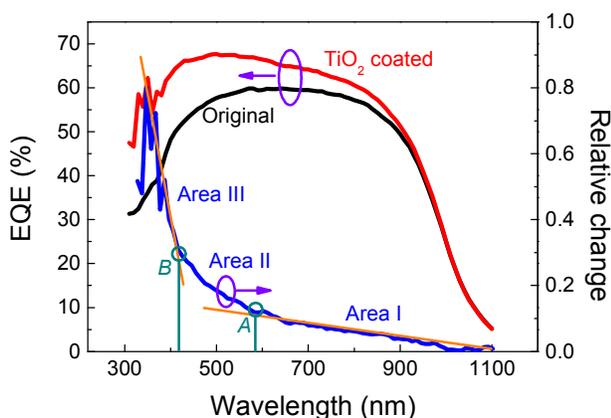


Figure 4. External quantum efficiency (EQE) of the device before and after TiO₂ coating. The blue curve shows the relative changes.

Similar to the MLG/Si side, the excited electron (e^-)-hole (h^+) pairs in TiO₂ layer should be separated by a suitable built-

in voltage. Thus the band structure of the TiO₂/MLG/Si system is critical to be investigated to support our analysis above. The band structure was investigated by a two-step method based on the C^2 - V measurements.

In detail, the band structures of TiO₂/MLG and MLG/Si were firstly measured individually and then combined to be a whole picture of the sandwich system, assuming that the weak influences between each other could be neglected. The measurements for TiO₂ NPs was based on a three-electrode system. TiO₂ NPs were spin-coated on an FTO coated glass and tested in 0.5 M H₂SO₄ aqueous solution. The result is shown in Figure 5a. By fitting the linear region of the C^2 - V plots, the x -intercept (V_0) was found to be -0.136 V.

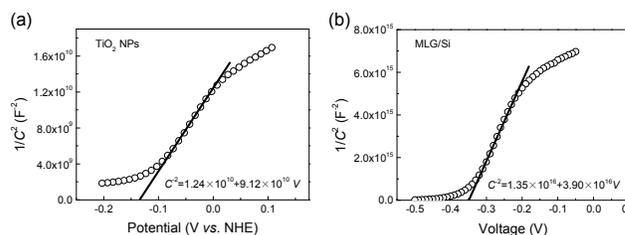


Figure 5. C^2 - V characteristics of (a) TiO₂ NPs and (b) MLG/Si Schottky diode.

Then the experimental carrier concentration and flat-band potential of TiO₂ NPs was calculated from the Mott-Schottky equation:⁴⁰

$$\frac{1}{C^2} = \left(\frac{2}{\epsilon_s q N_d A^2} \right) \left(V - V_{FB} - \frac{kT}{q} \right) \quad (1)$$

where C , ϵ_s , q , N_d , A , V , V_{FB} , k , and T are the space-charge capacitance, permittivity of the semiconductor ($48\epsilon_0$ for TiO₂), electron charge, experimental carrier concentration, effective area, applied bias, flat-band potential, Boltzmann's constant and absolute temperature, respectively. The value of N_{d,TiO_2} was found to be $1.03 \times 10^{20} \text{ cm}^{-3}$ and the flat-band potential V_{FB,TiO_2} (vs. NHE) was calculated by $V_{FB,TiO_2} = V_0 - kT/q = -0.162 \text{ V}$. As the V_{NHE} was about 4.5 V below the vacuum energy level, which was consistent with the work function of graphene ($\sim 4.5 \text{ eV}$),^{41,42} thus the V_{FB} (vs. graphene) was numerically identical to the V_{FB} (vs. NHE). Then, the width of the depletion layer was given by

$$W_{sc,TiO_2} = \sqrt{\frac{2\epsilon_s V_{bi}}{qN_d}} \quad (2)$$

The calculated W_{sc,TiO_2} was 2.89 nm. The potential change along the thickness direction of depletion layer was also confirmed by

$$V(x) = \frac{qN_d}{2\epsilon_s} (x + W_{sc})^2 \quad (3)$$

Then the band structure of TiO₂/graphene was deduced as shown in the left part of Figure 6a. To measure the C^2 - V characteristics of MLG/Si side, both the reference electrode and

counter electrode were connected with MLG, while the working electrode was connected with the back electrode of the device. By the same way, $N_{d,Si}$, $V_{FB,Si}$ and $W_{sc,Si}$ were calculated to be $3.08 \times 10^{16} \text{ cm}^{-3}$, -0.373 V and 125.5 nm , respectively. The $V(x)$ in MLG/Si side was calculated by Eq. 3. Therefore, the band diagram of the whole $\text{TiO}_2/\text{MLG}/\text{Si}$ system was deduced and is shown in Figure 6a.

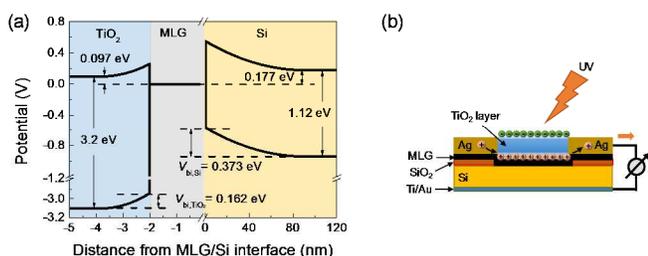


Figure 6. (a) Band diagram of the $\text{TiO}_2/\text{MLG}/\text{Si}$ system. (b) Schematic of the performance enhancement mechanism by TiO_2 coating.

It can be seen that there are two built-in voltages exist in the $\text{TiO}_2/\text{MLG}/\text{Si}$ system: one lies on the TiO_2/MLG interface, another lies on the MLG/Si interface. Once the incident light arrived at the TiO_2 layer, photons with energy higher than the band gap of TiO_2 was absorbed to excite the electrons of TiO_2 from its valance band to the conduction band, then the photo-generated electron-hole pairs were separated by the built-in voltage. The photo-generated holes (h^+) can be transport towards graphene together with the current generated from the MLG/Si side to the external circuit. However, as TiO_2 is a wide band gap dielectric material with poor conductivity, the photo-generated electrons (e^-) have to remain in the TiO_2 layer through capacitive coupling with the holes (Figure 6b), which is similar to the model presented before for graphene-quantum dot phototransistor.⁴³ Despite the carriers concentration of TiO_2 was much high than that of silicon, its enhancement effect might be limited by such mechanism, because too much electrons accumulated on the surface of the TiO_2 layer would enhance their recombination with the holes.

Conclusions

In summary, TiO_2 NPs was synthesized to enhance the ultraviolet photoelectrical conversion of the MLG/Si diode. After being coated by TiO_2 NPs, the PCE of the device was obviously improved (increased by 72.7% and 100% at 420 nm and 350 nm respectively). The EQE characteristics revealed that the enhancement mechanism of TiO_2 layer in the ultraviolet region was different from the long-wave region. Next, band diagram of the $\text{TiO}_2/\text{MLG}/\text{Si}$ system was established using the Mott-Schottky theory according to their $C^{-2}-V$ characteristics, which confirmed that there were two reciprocal Schottky junctions existed in the sandwich system. The enhancement mechanism was finally attributed to the carriers injection from the TiO_2 layer to the loop current of graphene/semiconductor based on the electronic band structure.

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†Electronic Supplementary Information (ESI) available: Transmission spectrum of graphene, XPS spectrum of graphene, $J-V$ characteristics and detection performance of the device. See DOI: 10.1039/b000000x/

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Graphic abstract

TiO₂ nanoparticles are spin-coated on the graphene/Si Schottky junction to improve its photoresponse in the ultraviolet region.

