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Photoresponsivity of silver nanoparticles decorated graphene-silicon Schottky junction

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Abstract

Here, we demonstrate formation of the silver nanoparticles (Ag-NPs) on chemical vapor deposited graphene by dissolving base Ag foil and their integration for Schottky junction photodetector fabrication. Ag-NPs of the size 20-100 nm were directly obtained by dissolving the Ag foil of as-synthesized graphene in a diluted HNO_3 solution. A Schottky junction is fabricated by transferring the Ag-NPs incorporated graphene onto Si substrate. In the fabricated device, significant photoresponse is

observed with illumination of 3.6, 5.1 and 2.1 mW/cm^2 of near-infrared (1000 nm), visible (550 nm) and near ultraviolet (350 nm) light, respectively. The graphene-Si Schottky junction shows photoresponse of 122, 98 and 78 mAW^{-1} at 550, 350 and 1000 nm, respectively. The strong photoresponce can be attributed to light interaction with the plasmonic Ag-NPs and effective graphene-Si Schottky junction. Our finding shows that enhancing the light absorption with plasmonic nanoparticles weakest of incident light can be detected for a broad-wavelength range.

1. Introduction

Combination of graphene based materials with other conventional semiconductors are of great interest for solar cells, photodiode, barristors and photodetector applications.[1-6] Significant effort has been given to develop a Schottky junction device integrating graphene with Si, GaN, Ga and SiC.[4-11] In such type of Schottky junction devices, graphene does not only act as a transparent conductor but also facilitates photo-exciton dissociation and charge separation.[1,12] Graphene with significantly high carrier mobility can also provide efficient charge transportation. Schottky junction diodes have been fabricated by transferring a mechanically exfoliated and chemical vapor deposited graphene on p or n type Si wafer. Interestingly, work function or the Fermi energy of graphene can be controlled by introducing chemical dopant and thereby optimizing the junction potential.[2,13,14] Graphene with the significant electrical, optical properties and ability to tune the Fermi energy can be also ideal material to fabricate high performance broadband photodetectors.

Fabrication of graphene based photodetectors has been achieved by exploiting the absorption (monolayer graphene~2.3%) of incident light in a broad wavelength range and high mobility for ultrafast detection.[15-18] A photoresponsivity of around 10 mAW^{-1} has been achieved with graphene based photodetectors in a field-effect transistor (FET) configuration.[18-21] Recently, Zhang et al., reported significantly high photoresponsivity

in a monolayer graphene photodetector by introducing electron trapping centers and creating a bandgap.[22] However, optical absorption in a monolayer graphene can be still considerably low, which can be overcome with integration of surface plasmonic nanoparticles. Liu et al. has demonstrated multi-color photodetectors by integrating gold plasmonic nanostructures with graphene.[23] A maximum photoresponsivity of 6.1 mA W^{-1} at 514 nm wavelength is achieved with gold plasmonic nanoparticles, which is still quite low. Fabrication of photodetector with a simple device architecture and high light sensitivity can be critical for practical applications. In this aspect and contrast to previous reports, graphene based Schottky junction device with plasmonic metal nanoparticles can be a promising approach to achieve high photoresponsivity.

In what follows, we demonstrate fabrication of a Schottky junction photodetecotor with Ag-NPs decorated CVD synthesized graphene and n-Si. Ag-NPs were directly obtained on the CVD graphene by dissolving the base Ag foil in diluted HNO_3 without using any other reagents. Significant photoresponse is observed in near-infrared (IR), visible and near ultraviolet (UV) wavelengths, attributing to light interaction with the plasmonic Ag-NPs in the fabricated device.

2. Experimental

In this experiment commercially available Ag foil with a thickness of 30 μm and purity 99.98% was used for graphene synthesis by the thermal CVD technique. 10 mg of solid camphor ($C_{10}H_{16}O$) was used as carbon source for graphene synthesis. Graphene growth was carried out at 945 ^{o}C (below melting point~961.8^{o}C of Ag) in a tubular furnace with a gas composition of Ar and H_2. The flow rate of Ar and H_2 was optimized as 85 and 5 standard cubic centimeters per minute (sccm), respectively. The solid carbon source was slowly evaporated and introduced in the growth zone along with the Ar and H_2 gas mixture. Finally, the CVD furnace was gradually cooled down to room temperature under the flow of 80 sccm H_2. The base Ag foil used for graphene synthesis was dissolved in a diluted HNO_3 solution to create the surface assisted Ag-NPs on graphene. Graphene-Si Schottky junction photodetector was fabricated by transferring the Ag-NPs decorated graphene on Au electrode deposited SiO_2/n-Si substrates.

Synthesized graphene materials were characterized with NRS 3300 laser Raman spectrometer with a laser excitation energy of 532.08 nm. The optical microscopy studies were carried out with VHX-500 digital microscope. Scanning electron microscopy (SEM) studies were carried out with JEOL JSM 5600. Transmission Electron Microscope (TEM) images were taken by JEOL JEM 2100, operated at 200 kv

equipped with an element analyzer. The Au electrodes were deposited by thermal evaporation technique using ULVAC VPC-260F. Current density-voltage (J-V) and external quantum efficiency (EQE) characteristics measurements were carried out at room temperature (25 ºC) using a solar simulator (Bunkoukeiki Co. Ltd., Japan) in the dark and under illumination with air mass (AM) 1.5 simulated solar radiation. The time dependent photoresponse characteristics were measured using a xenon lamp unit (SM-25, Bunkoukeiki Co. Ltd., Japan) with a monochromator. Response time of the device is measured by using HZ-5000 of Hokuto Denko Co. Ltd.

3. Results and discussion

Synthesized carbon material on Ag foil was characterized by Raman spectroscopy and optical microscopy to confirm graphene growth. Figure 1a shows the Raman spectra of as-synthesized graphene by the atmospheric pressure CVD process. Most prominent peaks in the spectra are observed at 1346, 1584 and 2696 cm^{-1}, corresponding to disorder-induced D, graphitic G and second order 2D peak, respectively. Presence of a strong 2D peak confirmed growth of graphene on the Ag foil. Previously, we have demonstrated that synthesis of few-layer graphene is possible by the CVD process on a noncatalytic Ag foil in presence of H_2 gas.[24] Figure 1b shows an optical microscope image of the graphene synthesized Ag foil. Polycrystalline Ag grain of few microns and

grain boundaries are evidently visible. The Ag foil with micron order grain size contains graphene domain with different number of layers. Recently, decoupled graphene growth on single-crystal Ag(111) substrate has been also achieved by a CVD process using solid carbon source.[25] The possibility of synthesizing graphene on noncatlaytic Ag foil can be significant to open up new possibilities for application considering the interesting optical and electrical properties of Ag.

The base Ag foil used for graphene synthesis was dissolved in a diluted HNO_3 (25% concentration) solution as shown in figure 2. Prior to dissolving the Ag foil, graphene was coated with a poly(methyl methacrylate) (PMMA) layer to transfer on Si substrate without any structural distortion. We observed gradual dissolution of the Ag foil in acid solution and leading to nanoparticles formation on the graphene surface. HNO_3 is an oxidizing agent and will oxidize Ag metal to Ag^+ ions, itself being reduced to a lower oxidation state. Most of the Ag dissolved in the reaction process, where some nanoparticles were formed at the graphene sheets in the acid solution. In the Ag foil dissolving process, graphene sheets acts a supporting surface for nanoparticles formation without using any other reagents. Previously, facile one-pot synthesize of Ag-NPs and graphene composite with GO and $AgNO_3$ solution in presence of a reductant and stabilizer has been achieved.[26] The nanoparticles obtained in our

demonstrated process remain highly disperse on the graphene sheets. The one step approach to obtain Ag-NPs decorated graphene can be used for various device applications.

The formation of Ag-NPs in the graphene sheet was analyzed and confirmed by TEM studies. Figure 3a shows TEM image of a monolayer graphene synthesized on Ag foil by the CVD process, however, few-layer graphene formation is also observed. Figure 3b shows Ag-NPs formation in the CVD derived graphene by dissolving the base Ag substrate. Ag-NPs with a size distribution of 20-100 nm is uniformly coated in the graphene sheets. Most of the nanoparticles are roughly round in shape, whereas some of them are rectangular in shape. Inset of figure 3b shows a high resolution TEM (HRTEM) image of a round shape nanoparticle, presenting high crystalline nature. The crystalline structure is further studied by HRTEM analysis as shown in figure 3c. The lattice-fringe distance is measured as 0.24 nm, which corresponds to the spacing of (111) plane of cubic Ag. Further, the selected area electron diffraction (SAED) pattern of a nanoparticle shows excellent crystalline structure as shown in figure 3d. The SAED pattern spots can be indexed as the (111), (200), (220) and (311) plane for Ag cubic lattice structure.[27-29]

A Schottky junction device is fabricated with as-derived Ag-NPs coated graphene.

Figure 4a shows a schematic representation of the Ag-NPs decorated graphene-Si Schottky junction. An ohmic back contact was created with deposition of Au:Sn on Si surface. SiO_2 was patterned on the front side of the n-Si wafer for the Schottky junction fabrication with the transferred graphene. Incident light in the device transmits through the graphene and absorbs in the Si wafer to generate photo-exciton. At the same time, the Ag-NPs can enhance light absorption with the surface plasmonic effect. Figure 4b_c shows optical microscope and SEM image of the fabricated device, presenting the transferred graphene on Si substrate. The graphene is transferred such that it is extended from the bare Si to SiO_2 patterned surface. Efficient exciton dissociation and charge transportation can be achieved at the interface of graphene and Si. Previously, we have demonstrated formation of a suitable potential barrier at the graphene/n-Si junction for efficient charge separation.[12]

Figure 5a shows J-V characteristic of the graphene/n-Si heterojunction device under dark condition. Rectifying J-V characteristics and ohmic back contact confirm formation of a Schottky junction at the graphene/n-Si interface. Figure 5b shows a log plot of the dark light characteristic. The fabricated Schottky junction shows a good rectification characteristic with an 'on/off' ratio of around 10^2 at ±1 V. Photo-response properties of the fabricated graphene/n-Si Schottky junction were also investigated with

illumination of 100 mW/cm^2. Figure 5c shows J-V characteristic of the fabricated device with and without light illumination. A photovoltaic action with open circuit voltage (V_{oc}) 0.38 V, short circuit current density (J_{sc}) 3.5 mA/cm^2, fill factor (FF) of 20 % and conversion efficacy of 0.27 % is obtained. The photosensitivity and photovoltaic action in the fabricated device indicate photoexcitation of carriers and photocurrent generation at the graphene/n-Si interface. Figure 5d shows a quantum efficiency curve of the fabricated Schottky junction with Ag-NPs decorated graphene. We observe considerable phototresposnce and EQE in the shorter wavelength range as well, which can be attributed to the surface plasmon resonance scattering of Ag-NPs.

Photoresponsivity of the fabricated device was further investigated with illumination of different light intensities and wavelengths. Time-dependent photocurrent measurements are performed in the NIR (1000 nm), visible (550 nm) and near-UV (350 nm) wavelengths. Figure 6a-c shows time-dependent photocurrent of the fabricated device with illumination of 3.6, 5.1 and 2.1 mW/cm^2 light at 1000, 550 and 350 nm wavelengths. We observe significant on/off current with low illumination light intensity. The graphene/n-Si Schottky junction photodetector shows photoresponse of 78, 122 and 98 mAW^{-1} in the NIR, visible and near-UV, respectively. Previously, it has been reported observation of photoresponsively of about 10 mAW^{-1} in graphene based device

with an optical pumping as high as 10^8 mW/cm^2.[22] Recently, a maximum photoresponsively of 62.95 mAW^{-1} at 445 nm wavelength has been achieved in a reduced graphene oxide/Si heterojunction device.[30] Figure 6d shows a photoresponse curve measured with illumination at 550 nm wavelength. The photoresponse time in the fabricated device is measure to be around 2.85 ms, which is comparable to CVD graphene/Si based photodetectors.[5,30-33] Considering the previous findings, we demonstrate that Schottky junction fabricated with Ag-NPs decorated graphene and n-Si shows significant photoresposne at a quite low illumination intensity and zero bias voltage. Figure 6d shows a schematic cartoon of the fabricated device, illustrating the effect of plasmonic Ag-NPs on photoresponsivity. The strong photoresponce can be attributed to light interaction with the plasmonic Ag-NPs and formation of an efficient Schottky junction. The decorated Ag-NPs in the graphene can enhance near-field oscillation of conduction electrons and scattering of incident light. With oscillation, light can trapped around surface of Ag-NPs, leading to enhance local electrical field and thereby improving light absorption. Further enhancement of the overall photoresponsivity can be expected with higher quality graphene and optimized device structure and contact electrodes. Our finding can be significant to achieve high performance broad-band photodetecotors with plasmonic nanoparticles decorated

graphene Schottky junction devices.

Conclusion

We have demonstrated formation of Ag-NPs on a CVD synthesized graphene by dissolving the base Ag foil and their integration for Schottky junction fabrication. Ag-NPs of the size 20-100 nm were directly obtained on graphene surface by dissolving the Ag foil of as-synthesized graphene in a diluted HNO_3 solution. The Ag nanoparticles decorated graphene was transferred onto n-Si substrate for fabrication of a Schottky junction. Significant photoresponse was obtained in the device with illumination of 3.6, 5.1 and 2.1 mW/cm^2 of near-IR (1000 nm), visible (550 nm) and near-UV (350 nm) light, respectively. The Ag-NPs decorated graphene-Si Schottky junction showed photoresponse of 122, 98 and 78 mAW^{-1} at 550, 350 and 1000 nm, respectively. The strong photoresponce is attributed to light interaction with the plasmonic Ag-NPs and efficient Schottky junction formation. In the demonstrated device plasmonic Ag-NPs can enhance light absorption and thereby enabling detection of the faintest incident light for a broad-wavelength range.

Acknowledgement

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Figure captions

Figure 1 (a) Raman spectra and (b) optical microscope image of as-synthesized graphene on Ag foil by an atmospheric pressure CVD process.

Figure 2 Ag-NPs formation on the as-synthesized CVD graphene by dissolving base Ag foil in a diluted HNO_3 solution.

Figure 3 (a) TEM image at the edge of a graphene sheet synthesized on Ag foil by CVD process. (b) Formation of Ag-NPs decorated graphene by dissolving the Ag base substrate in a HNO_3 solution (inset shows a round shape Ag-NP) (c) HRTEM image and (d) SAED pattern of a Ag-NP, presenting high crystalline nature and cubic lattice structure.

Figure 4 (a) schematic diagram of the fabricated Schottky junction with the transferred Ag-NPs incorporated graphene on n-Si substrate. (b) Optical microscope and (c) SEM images of Ag-NPs coated graphene transferred to the SiO_2 patterned Si substrate.

Figure 5 (a) J-V characteristic of the graphene/n-Si heterojunction and (b) log plot under dark condition. (c) J-V characteristic of the fabricated device with (100 mW/cm^2) and without light illumination. (d) EQE of the fabricated Schottky junction.

Figure 6 Time-dependent photocurrent of the fabricated device with illumination of 5.1, 3.6 and 2.1 mW/cm^2 light at (a) 550 (b) 1000 and (c) 350 nm wavelengths. The

graphene/n-Si Schottky junction photodetector shows photoresponse of (a) 122 (b) 98 and (c) 78 mAW^{-1} in the visible, near-UV and NIR, respectively. (d) Response time with illumination at 550 nm wavelength. (d) Schematic cartoon of the fabricated device, illustrating the effect of plasmonic Ag-NPs on photoresponsivity.

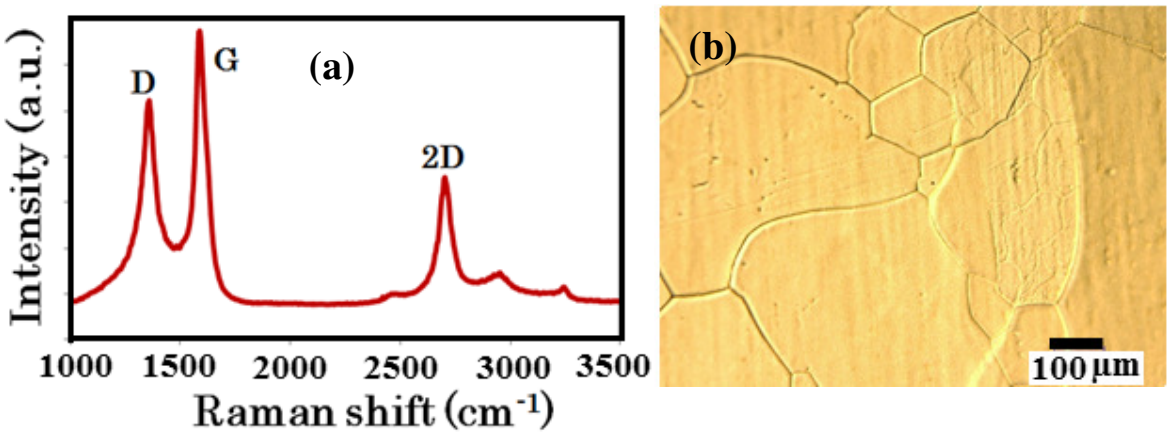
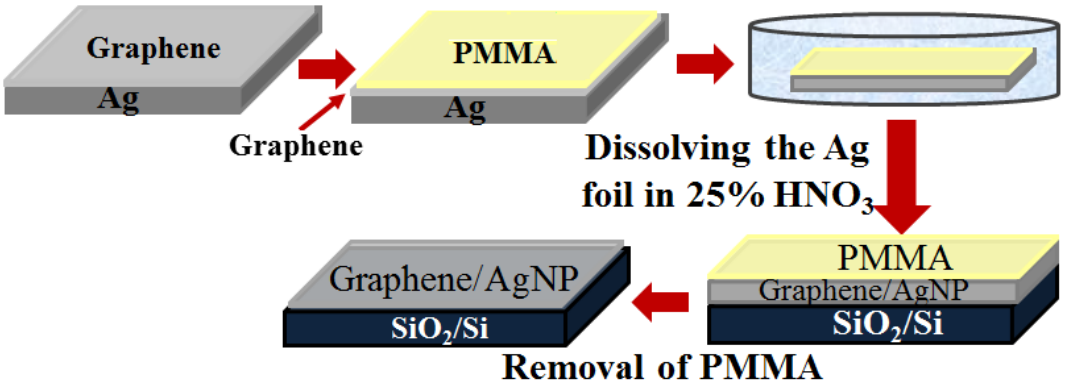


Figure 1



$$2Ag(s) + 2HNO_3(aq) \rightarrow 2AgNO_3(aq) + H_2(g)$$

Figure 2

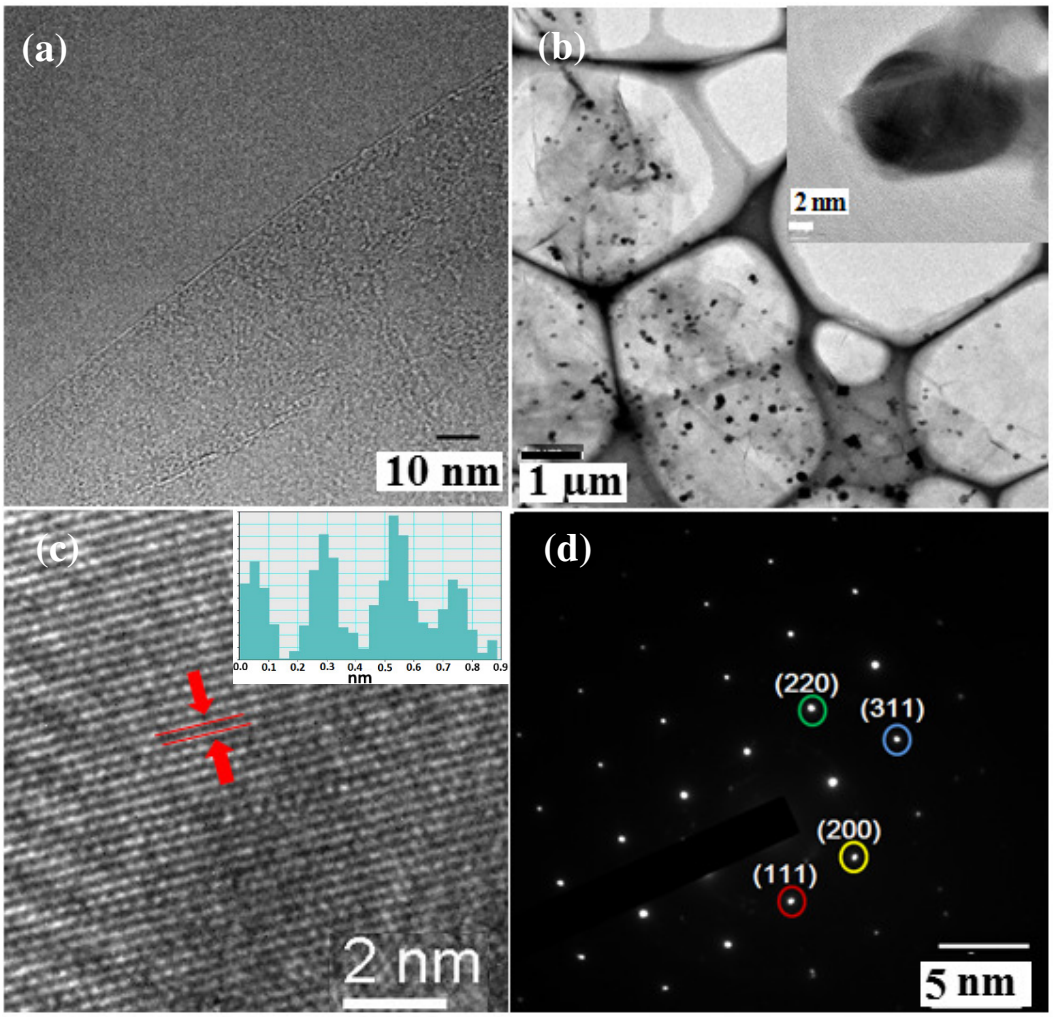


Figure 3

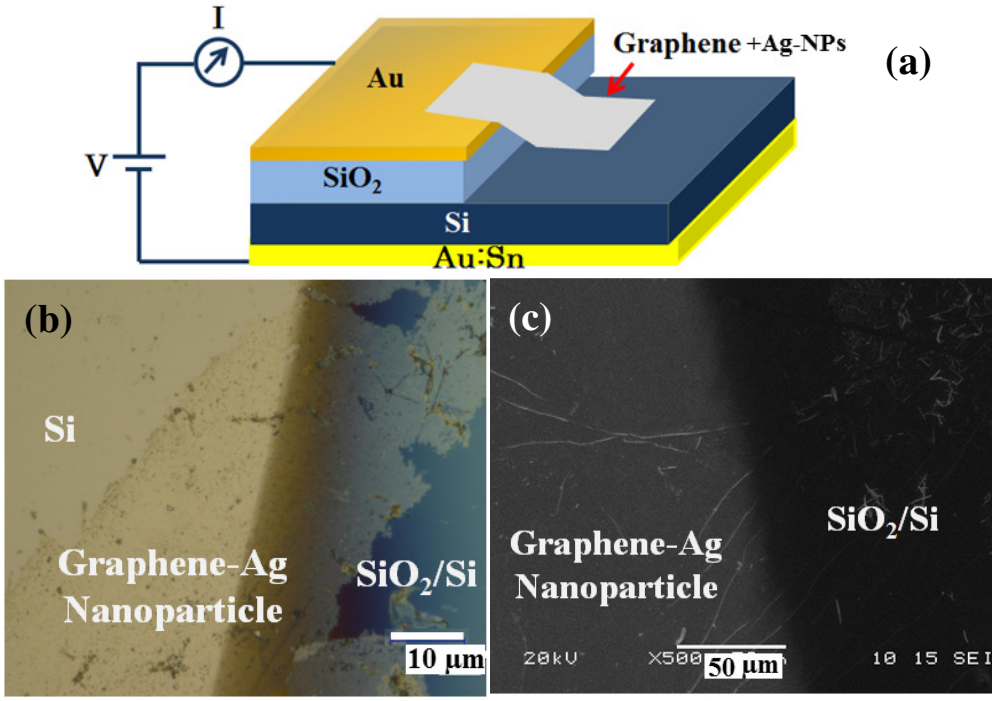


Figure 4

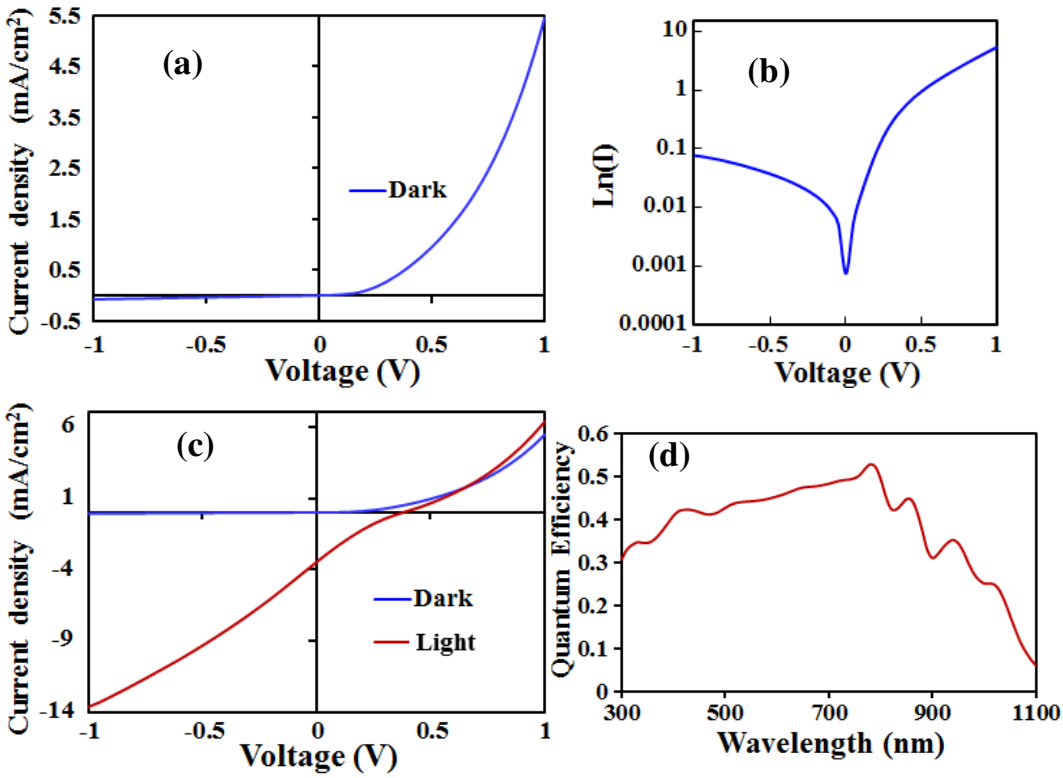


Figure 5

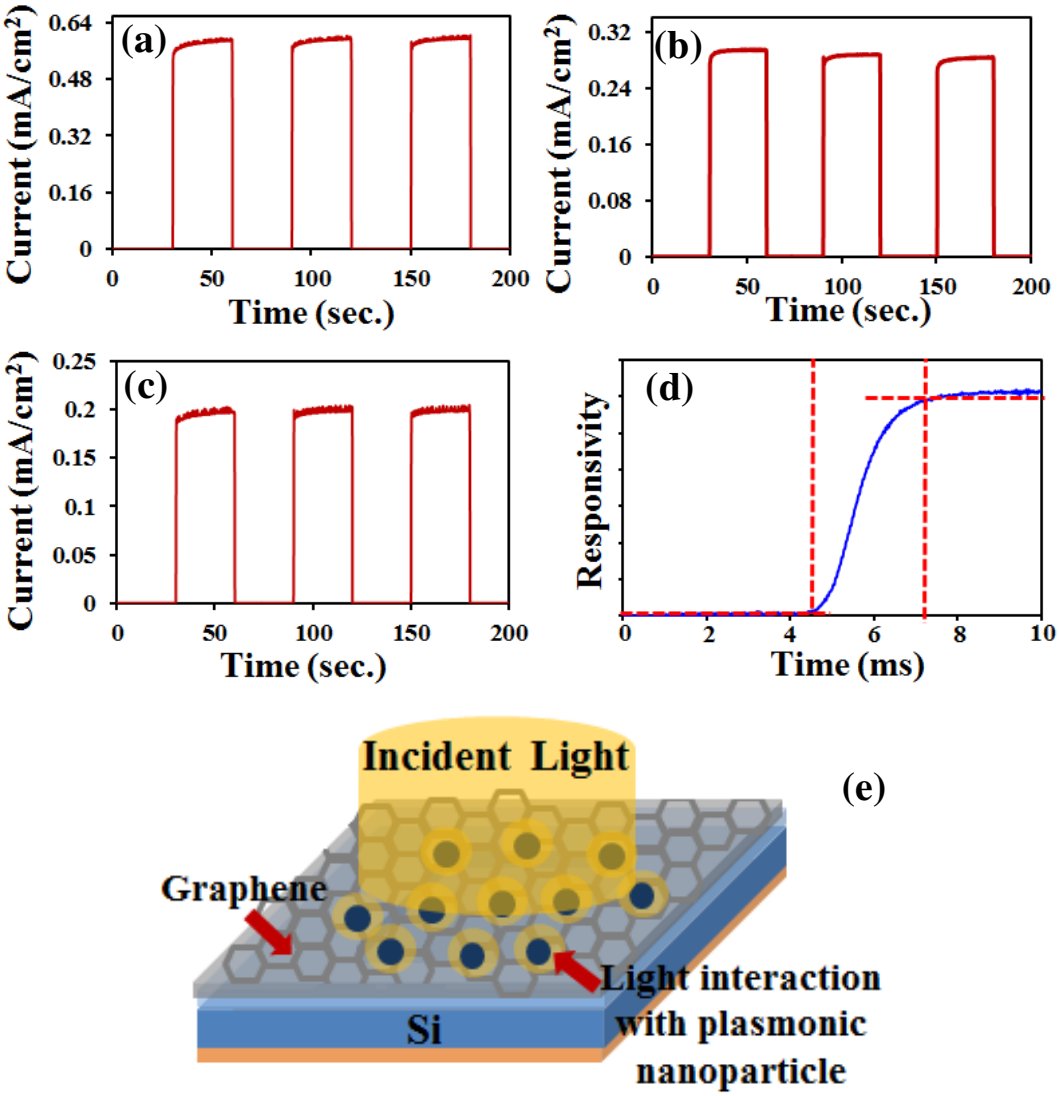


Figure 6