VOL. 20, NO. 2-2, 2021, 77-81
www.elektrika.utm.my
ISSN 0128-4428

ELEKTRIKA
Journal of Electrical Engineering

Development of High Photosensitive Gold Nanorods/Zinc Oxide Photodetector

Chi-Shen Lin and **Wei-Chih Lin***

Department of Mechanical and Electro-Mechanical Engineering, National Sun Yat-sen University, Kaohsiung, Taiwan

*Corresponding author: wc.lin@mail.nsysu.edu.tw, Tel: (07)525-2000 # 4462

Abstract: In this study, we present a development and fabrication of the plasmonic ultraviolet Gold nanorods (GNRs)/zinc oxide photodetector (ZnO PD) by using the micro-fabrication technique. The synthesis of GNRs is based on the seed-mediated method and the length and diameter of synthesized GNRs are approximate 13±2.3 nm and 50±6.4 nm. After decorating GNRs to the ZnO PD by using spin coating, the on/off ratio of ZnO PD is increased from 9.8 to 70. The enhancement mechanism is attributed to the formation of a local Schottky interface in the metal-semiconductor interface and the LSPR effect can generate the hot electrons and enhance the light scattering. Furthermore, the μ-PL is applied to separate analyse the optical properties of ZnO and GNRs/ZnO film. The near band emission is significantly enhanced, and the defect emission is also suppressed by decorating GNRs on the surface of the ZnO film. The experiment results indicate that decorated GNRs on the surface of ZnO can improve the performance of the ZnO PD. Therefore, GNRs material has a high protentional to improve the photosensitivity of the ZnO PD for photocatalysis and optoelectronic applications.

Keywords: Photodetector, Localized, surface plasmon resonance, Gold nanorod, Zinc oxide

Article History: received 25 May 2021; accepted 12 June 2021; published 15 September 2021.

1. INTRODUCTION

Ultraviolet photodetectors (UV PDs) have drawn extensive attention mostly because of its diverse application possibilities [1-3]. For example, in the semiconductor industry, UV PDs have been widely used for photocuring, packaging and mass transfers. In all these applications, an ideal UV PDs should have high sensitivity and high light-to-dark current ratio in the ultraviolet spectral region. The dark current must be kept low while seeking high photo responses in order to warranty sufficient noise suppression.

Recently, many wide band gap nanostructured materials have been used for this purpose to fabricate high performance light sensors, including silicon carbide (SiC), gallium nitride (GaN), and zinc oxide (ZnO), among others. The ZnO of Wurtzite crystal structure is an oxide semiconductor with a wide direct energy gap of ~3.37 eV that is ideal, similar to GaN, for light sensing in the UV-A region. It has an exciton binding energy of ~60 meV that is more than twice the 25 meV for GaN [4]. At room temperature, the thermal excitation energy is only about 25 meV, insufficient to annihilate the electron-hole pairs in ZnO. This large exciton biding energy this translates directly into higher performance various photoelectronic devices. Demonstrated excellent photoelectric performance, low threshold current, ease of manufacturing into nanostructures, and environmental friendliness, coupled with its multi-functional properties that include the well-known piezoelectricity, have all contributed to making ZnO one of the most sought-after semiconductor materials for UV PDs [3, 5-7]. ZnO tends to exist with inherent defects or impurities. This would increase the absorption of visible or any light in the sub-UV regions and reduce the performance of a photoelectronic ZnO device. Therefore, there are still challenges faced in developing high performance of UV sensors [8-10]. Many approaches have been taken to enhance the sensitivity of the UV PDs. These include extrinsic doping, use of quantum dots, and metal nanostructure-incurred local surface plasmon resonance (LSPR). The LSPR effect has proven to be an effective simple approach to bypassing inherent material defects problems of semiconductors for performance improvements of associated optoelectronic devices [11-13], as has been seen in enhanced optical absorptions.

Plasmon metal nanomaterials are excited by local surface plasmon resonance (LSPR), which is characterized by strong interactions with electromagnetic radiation, e.g., photons. At the resonance frequency of the nanorods enhanced surface results in increased electric field of the light-matter interaction. The increased magnetic field produces more high-energy charge carriers (electron-hole pairs), by the energetic charge carriers is attached to the reactant adsorbed on the surface of the nanostructures. Guidelli et al. Reported that when excited at 325nm, both ZnO/Ag and ZnO/Au particles showed significantly enhanced near-band edge UV emission of ZnO [14]. Pescaglini et al. first presented photodetectors constituting GNRs-ZnO nanowire hybrid systems. The hot electrons generated by the LSPR of GNRs are injected into ZnO nanowires. They achieved one order of magnitude faster than the ZnO response under radiation above band gap [15].

In this work, we synthesize PEGylated GNRs and decorate them onto the planar ZnO UV PD via the spin coating process for achieving the fabrication of PEGylated GNRs/ZnO UV PD. The micro-photoluminescence

spectrum (μ-PL) is utilized to study the electron transitions between energy levels of GNRs and ZnO. The semiconductor device analyser is used to separately measure the photocurrent properties of ZnO PDs and PEGylated GNRs/ZnO PDs under dark and UV irradiation conditions.

2. FORMATTING

2.1 Fabrication of GNRs/ZnO PD

The structure of ZnO PD is Metal-Oxide-Semiconductor Field-Effect Transistor (MOS FET) structure by using several micro-fabrication processes, as shown in Figure 1. The fabrication starts with clean n-type Si_3N_4/Si substrate. The substrate was cleaned by standard wet cleaning, and the pattern was defined according to the standard optical lithography procedure, and ZnO was deposited by radio frequency (RF) sputtering with argon oxygen ratio of 1:10 at power 100 W. The production of the electrode uses the same photolithography procedure, and the metal contact of Al was deposited at 300 W power. After the fabrication of ZnO PDs, 50 μL of purified PEGylated GNRs were dropped into the sensing zone of ZnO, and then coated with two-stage spin coating at 300 rpm for 20 seconds and 2000 rpm for 120 seconds for uniform coating and solvent volatilization volatilize the solvent.

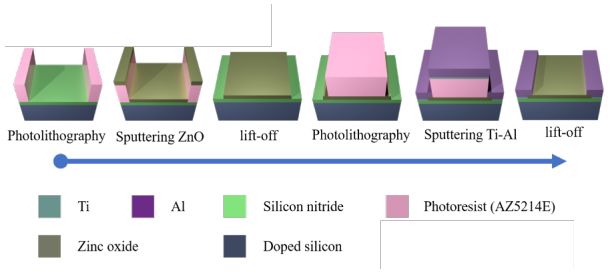

Figure 1. Schematic figures describe fabrication ZnO photodetector process charts.

2.2 Synthesis and Purification of gold nanorods

GNRs synthesis was using a seed-mediated method, reported by Khanal et al. [16]. In order to purify GNRs, GNRs were used for third centrifugations to achieve purification and shape separation. The PEGylated GNRs solution was prepared by following the standard procedure reported by Du et al. [17].

2.3 Measurement of material characterization and photoelectric properties

The micrograph image was performed by Transmission electron microscope (JEOL 3010 TEM, Japan). The optical properties of GNRs were measured by UV-Vis spectrophotometer (Hitachi U-4100, Japan). The representative ZnO FET device microscope image was captured by scanning electron microscope (SEM, Zeiss Supra 55, Germany). The optical properties of GNRs/ZnO were studied by micro-photoluminescence (μ-PL) with 325 nm continuous wave (CW) laser as excitation source (HORIBA HR800, Japan). Electrical characterizations of the ZnO PDs were measured with a semiconductor device analyser (Agilent B1500, USA) by an optical microscopy platform.

3. RESULTS AND DISCUSSION

The average length and diameter of the PEGylated GNRs are about 13±2.3 nm: 50±6.4 nm, i.e., at an aspect ratio of 3.84, as seen by TEM imaging of the synthesized PEGylated GNRs shown in Figure 2 (a). These samples exhibit two typical LSPR peaks in the optical absorption spectra around 514 nm and 763 nm, as shown in Figure 2 (b). The two resonance bands are associated with the free electrons oscillating along the transverse and longitudinal directions of the GNRs. The 514 nm peak correspond to the transverse mode, while the longitudinal mode occurs at 763 nm. The longitudinal mode is usually found to arise at a longer wavelength and strongly depend on the aspect ratio of GNRs, with increasing of GNRs aspect ratio, the wavelength of longitudinal LSPR would shift to a longer wavelength [18].

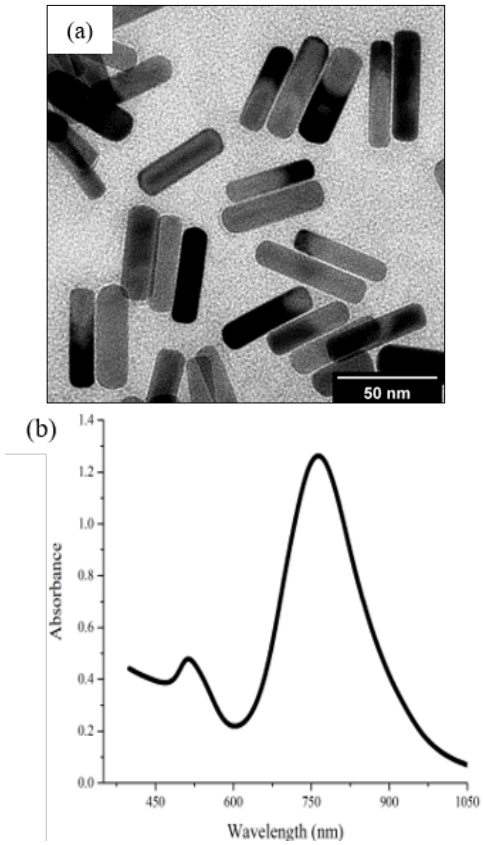

Figure 2. (a) The TEM micrography presents synthesised PEGylated GNRs, (b) UV-Vis absorption spectra of PEGylated GNRs solution.

Figure 3 (a) and (b) the representative SEM image of the ZnO film and GNRs/ZnO film, respectively. Figure 4 (a) shows μ-PL spectrum which was obtained from the measurement of the deposited ZnO film and PEGylated GNRs/ZnO film. While the NBE emissions happens largely at the similar wavelength for both the decorated and undecorated samples, the defect-related yellow emissions are notably suppressed for that which is decorated. The defect related visible emission band is produced by the recombination between electrons of defect level and holes in VB.

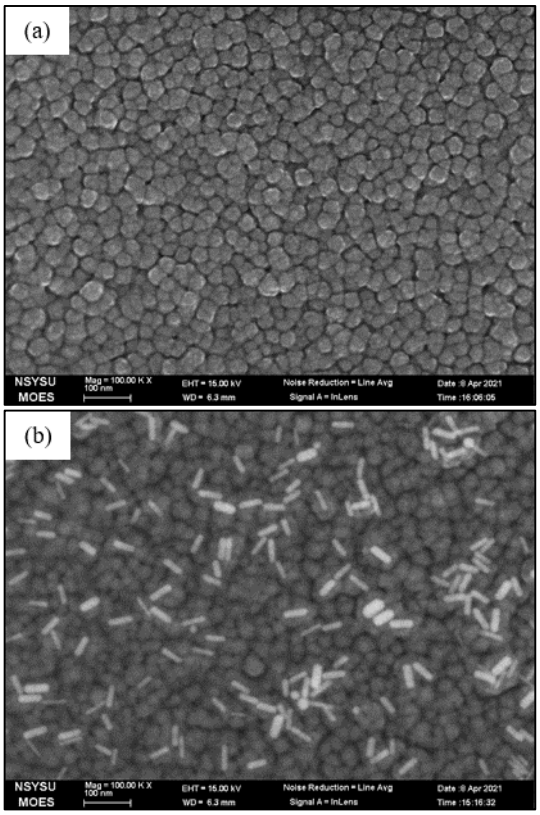

Figure 3. SEM image of (a) ZnO film and (b) PEGylated GNRs/ZnO film.

Coincidentally, the photon energy emitted by defects is very close to the LSPR energy of GNRs in previously studied (Figure 2 (b). Therefore, GNRs can be used as an excellent absorbent of defect emission (see Figure 4 (b)). The defect luminescence (DL) generated by ZnO is resonantly absorbed by GNRs. After LSPR is stimulated, the non-radiative decays into hot electrons, especially the hot carriers that transfer from the high-energy GNRs electron energy level to the high-energy ZnO conduction band (CB) state, which thermalize to the NBE. The radiative recombination of these CB electrons with free holes in the valence band (VB) enhances the UV excitonic emission. In other words, the NBE is greatly enhanced by the effect of LSPR excited by defect emission [13].

The intensity of the NBE of the GNRs-decorated sample is significantly increased by about 4.5 times. The enhancement of NBE indicates the tendency to radiative recombination of the electrons and holes in the presence of the gold NPs atop the ZnO film [35]. The LSPR becomes an excited state when light is incident on these interacting films, and the light scattering increases the travel length of the light on the GNRs/ZnO surface. As the scattering and absorption increase, the efficiency of photon injection into the semiconductor interface becomes higher. Therefore, LSPR of GNR with high radiation performance will induce local electric field enhancement around the coupling region, thereby enhancing the formation of electron-hole pairs. This could be associated with a longer lifetime of the photo-generated carriers caused by the charge transfer between the GNRs and the ZnO films in creation of a Schottky barrier with a built-in electric field and a depletion region.

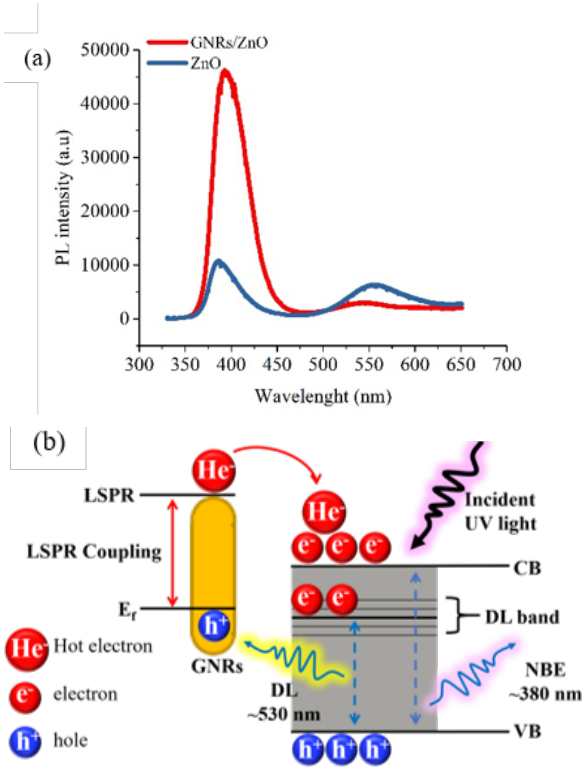

Figure 4. (a) the μ-PL spectrum measured from the ZnO film and GNRs/ZnO film, (b) schematic diagram for the proposed enhancement mechanism of carrier generation and recombination between GNRs and ZnO film.

The schematic figure of I-V characteristics of GNRs/ZnO photodetector and enhancement mechanism is show in Figure 5 (a). In the dark environment, the oxygen is adsorbed on the surface of ZnO film, which consumes electrons to form O_2^-, thus forming a low-conductivity depletion region on the surface. This reaction kinetics on the ZnO surface can be expressed as equation(1) [19].

$$O_2(g) + e^- \rightarrow O_2^-(ad) \quad (1)$$

After the GNRs are decorated, the local Schottky interface is formed at the junction, which expands the charge-depletion region due to the different work functions of GNRs (5.1 eV) and ZnO (4.45 eV). Under UV irradiation, the light-generated holes will migrate to the surface, thereby releasing adsorbed O_2^-, which leads to an increase in the concentration of free carriers and a decrease in the width of the depletion layer. This reaction kinetics on the ZnO surface can be expressed as equation (2)and (3) [19].

$$h\upsilon \rightarrow e^- + h^+ \quad (2)$$

$$h^+ + O_2^-(ad) \rightarrow O_2(g) \quad (3)$$

Figure 5 (b) shows that the GNRs/ZnO photodetector stimulates the LSPR effect under UV irradiation, thus reducing the charge depletion region and inducing light scattering to form a double enhancement. The photoconductive behaviour of GNRs/ZnO FET

Photodetector was investigated. At room temperature in ambient conditions. Figure 5 (c) and (d) showed I-V characteristics of ZnO PD with and without GNRs both in darkroom and incident with UV radiation at 375 nm. The I-V characteristic curve is nonlinear, which shows that hybrid photodetector is representative Schottky contacts.

At 15V bias, the dark current of the devices with and without GNR are 5.9 nA and 16.4 nA. respectively. After decorated, the dark current of GNRs/ZnO PD was decreased by 2.8 times. This phenomenon is caused by the contact of GNRs on the surface of ZnO film. Due to the different work functions of GNR and ZnO, which were depleted the carriers near the surface of ZnO, thus expanding the width of the charge depletion region. However, under UV light, the photocurrent with and without GNR are 410 nA and 160 nA, respectively. The photocurrents of the GNR/ZnO PD was increased more than 2.6 times, which was significantly increases due to the hot electrons generated by the LSPR of GNRs are injected into ZnO. When metal nanostructures were exposed to light radiation, GNRs will undergo LSPR excitation and plasma decay processes. During the decay process, the accumulated energy in the conduction band of the material are transferred to electrons, which will generate high-energy electrons and collect them through the contact between GNRs and ZnO interfaces, forming a typical Schottky contact. Another reason is that GNR enhances the scattering of light, thus enhancing the absorption of light on the ZnO surface. Based on the double enhancement, the ratio of light to dark current is increased from 9.8 up to 70 to achieve a high on/off ratio UV PD.

In order to better understand the mechanism at the interface of these performance enhancements, the photoconductive behaviour observed in UV photodetector is attributed to the generation of plasmon-mediated hot electron and injection at the interface of the GNRs-ZnO film. The schematically depict a theoretical model of hot electron injection energy band schematic, Figure 6 (a) depicts the conduction band electrons in gold nanorods induced by LSPR with parabolic state density (DOS). Fermi energy is a function of energy. where incident radiation excites local surface plasmons in GNRs. After excitation show in Figure 6 (b), local surface plasmons can be non-radiatively decayed by transferring energy to electrons, resulting in a "hot electron" distribution, which is much higher than the metal's Fermi energy. Electrons with higher energy than Schottky's potential base at the metal-semiconductor interface are injected directly into the conductor band of the ZnO, which proves to assist in enhancing the generation of photocurrent according to previous experimental results.

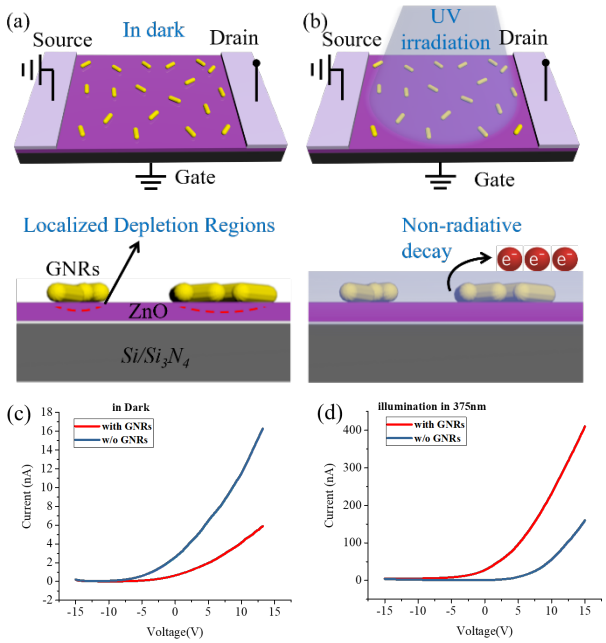

Figure 5. I-V characteristics of GNRs/ZnO PD and ZnO PD, (a) in dark condition and (b) under UV light irradiate at 365 nm.

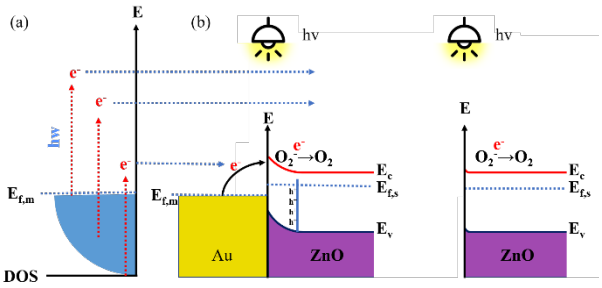

Figure 6. The hot-electron generation and injection processes at the GNRs -ZnO and bare ZnO interface. (a) LSPR induced energy distribution of the electrons in Gold nanorod. (b) Energy band diagram of GNRs -ZnO and bare ZnO

4. CONCLUSION

In conclusion, GNRs were successfully synthesized by using the seed-mediated method and the LSPR effect of GNRs can enhance the photosensitivity of the ZnO PD. We utilized the μ-PL to separately study the optical properties of bare ZnO and GNRs/ZnO film. Compared with bare ZnO film, the band edge emission of GNRs decorated ZnO film is increased by around 4.5 times and the emission in the visible region can be suppressed. Moreover, the photocurrent and the on/off ratio is increased by 2.6 times and 7 times, respectively. The enhancement of plasmon photocatalysis is attributed to two mechanisms : (i) the formation of a local Schottky interface on the metal-semiconductor interface that can assistive to reduce the dark current and promoting the electron-electric separation. (ii) The LSPR effect generates hot electrons and enhances light scattering. Therefore, this development of GNRs/ZnO PD has a high possibility for applications, such as photodetectors, photoelectric sensors and photovoltaic devices.

ACKNOWLEDGMENT

The author would like to acknowledge National Sun Yat-sen University, Kaohsiung, Taiwan for supporting this work.

REFERENCES

[1] E. Monroy, F. Omn s, F. Calle, "Wide-bandgap semiconductor ultraviolet photodetectors," *Semicond Sci Technol*, 18 (2003) pp. R33-R51.

[2] Y. Zou, Y. Zhang, Y. Hu, H. Gu, "Ultraviolet detectors based on wide bandgap semiconductor nanowire: A review," *Sensors (Basel)*, 18 (2018).

[3] Ü. Özgür, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.J. Cho, H. Morkoç, "A comprehensive review of zno materials and devices," *J Appl Phys*, 98(2005) pp. 041301.

[4] D. G. Thomas, "The exciton spectrum of zinc oxide, J Phys Chem Solids, 15(1960) pp. 86-96.

[5] A. Janotti, C.G. Van de Walle, "Fundamentals of zinc oxide as a semiconductor," *Rep Prog Phys*, 72 (2009) pp. 126501.

[6] H.-Y. Chen, K.-W. Liu, X. Chen, Z.-Z. Zhang, M.-M. Fan, M.-M. Jiang, X.-H. Xie, H.-F. Zhao, D.-Z. Shen, "Realization of a self-powered zno msm uv photodetector with high responsivity using an asymmetric pair of au electrodes," *Journal of Materials Chemistry C*, 2 (2014) pp. 9689-9694.

[7] K. Liu, M. Sakurai, M. Aono, "Zno-based ultraviolet photodetectors, *Sensors*," 10 (2010).

[8] H. Chen, K. Liu, L. Hu, A.A. Al-Ghamdi, X. Fang, "New concept ultraviolet photodetectors," *Materials Today*, 18 (2015) pp. 493-502.

[9] G. M. Ali, P. Chakrabarti, "Effect of thermal treatment on the performance of zno based metal-insulator-semiconductor ultraviolet photodetectors," *Appl Phys Lett*, 97 (2010) pp. 031116.

[10] K.-H. Bang, D.-K. Hwang, J.-M. Myoung, "Effects of zno buffer layer thickness on properties of zno thin films deposited by radio-frequency magnetron sputtering," *Appl Surf Sci*, 207 (2003) pp. 359-364.

[11] J.-A. Huang, L.-B. Luo, "Low-dimensional plasmonic photodetectors: Recent progress and future opportunities," *Adv Opt Mater*, 6 (2018) pp. 1701282.

[12] J. Lu, Z. Shi, Y. Wang, Y. Lin, Q. Zhu, Z. Tian, J. Dai, S. Wang, C. Xu, "Plasmon-enhanced electrically light-emitting from zno nanorod arrays/p-gan heterostructure devices," *Sci Rep*, 6(2016) pp. 25645.

[13] C.W. Cheng, E. J. Sie, B. Liu, C. H. A. Huan, T.C. Sum, H.D. Sun, H.J. Fan, "Surface plasmon enhanced band edge luminescence of zno nanorods by capping au nanoparticles," *Appl Phys Lett*, 96 (2010) pp. 071107.

[14] E. J. Guidelli, O. Baffa, D. R. Clarke, "Enhanced uv emission from silver/zno and gold/zno core-shell nanoparticles: Photoluminescence, radioluminescence, and optically stimulated luminescence," *Sci Rep*, 5 (2015) pp. 14004.

[15] A. Pescaglini, A. Martín, D. Cammi, G. Juska, C. Ronning, E. Pelucchi, D. Iacopino, "Hot-electron injection in au nanorod–zno nanowire hybrid device for near-infrared photodetection," *Nano Lett*, 14 (2014) pp. 6202-6209.

[16] B. P. Khanal, E. R. Zubarev, "Rings of nanorods," *Angew Chem Int Ed*, 46(2007) pp. 2195-2198.

[17] X. Du, W.-C. Lin, Q. Shou, X. Liang, H. Liu, "Ph optimization for high-efficiency pegylation of gold nanorods," *Colloid and Polymer Science*, 297 (2019) pp. 891-902.

[18] L. Tong, Q. Wei, A. Wei, J. X. Cheng, "Gold nanorods as contrast agents for biological imaging: Optical properties, surface conjugation and photothermal effects," *Photochem Photobiol*, 85 (2009) pp. 21-32.

[19] Y. Takahashi, M. Kanamori, A. Kondoh, H. Minoura, Y. Ohya, "Photoconductivity of ultrathin zinc oxide films," *Jpn J Appl Phys*, 33 (1994) pp. 6611-6615.