

# Enhanced and Tunable Absorption Characteristics of Au-nanoparticle Loaded ZnO Nanorods Grown by Hydrothermal Technique

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**Abstract**— In this work we report materials growth, optical characterization and finite-difference time domain (FDTD) based numerical analysis to study the enhancement and tuning of absorption characteristics of gold nanoparticle loaded ZnO nanorods grown by hydrothermal technique. Scanning electron microscopy imaging confirms that nearly vertically oriented, ordered array of ZnO nanorods can be grown on glass substrates if prior to hydrothermal growth, a seed layer of Al-doped ZnO (AZO) is deposited onto the substrate using drop-casting technique. Optical spectroscopy confirms absorption enhancement of the array with increasing size of gold-nanoparticles attached to the ZnO nanorods. Numerical results obtained from FDTD analysis of the three-dimensional photonic structure confirm that the reduced transmittance observed at ~550 nm is owing to the absorption enhancement caused by plasmonic resonance of the Au-nanoparticles. The simulation results also show that absorption characteristics of such arrays can be conveniently tuned from visible to near-infra-red wavelengths by controlling diameter and areal density of the nanorods. This study also suggests future scopes of research in this area regarding further enhancement and tuning of absorption characteristics of nanoparticle loaded ZnO nanorods grown on an AZO seeded substrate by hydrothermal technique.

**Keywords**— Hydrothermal growth, drop-casting technique, nanorod, plasmonic, finite-difference time domain simulation, absorbance, transmittance

## I. INTRODUCTION

Zinc Oxide (ZnO) is one of the most widely studied semiconducting metal oxide owing to its large direct bandgap of 3.37eV and remarkably high exciton binding energy of 60 meV at room temperature. These exotic properties, along with its numerous functionalities, make ZnO a promising material for applications related to optoelectronics, sensing, photovoltaics and lasing [1, 2]. The capability of fabricating devices using both bottom-up or top-down techniques based on epitaxially grown, chemically synthesized, or physically deposited thick/thin-films and nanostructures have further broadened the breadth of applications of this material system

[3-6]. Among different low-dimensional structures of ZnO, nanowires (NWs)/nanorods (NRs) have gained considerable attention owing to their unique electrical, optical and mechanical properties compared to the bulk counterparts [7-9]. Synthesis and characterization of *c*-axis oriented ordered arrays of ZnO NRs is considered to be particularly important for the efficient transport and collection of carriers pertaining to photovoltaic energy harvesting and photo-detection related applications [10, 11]. Among different reported techniques of ZnO NR growth and deposition, the hydrothermal technique deserves attention because of its cost-effectiveness, repeatability, and environment-friendly nature [12, 13]. By controlling different growth parameters of this technique, the diameter and density of NRs can be appreciably controlled – an aspect which should offer significantly tunability of absorption characteristics of the NR-array. Moreover, by loading the NRs with metallic nanoparticles, plasmonic effects can be incorporated into such structures to further tune and enhance the overall absorption characteristics of the material system.

In the present study, we employ experiments and simulations to study transmission and absorption characteristics of *c*-axis oriented, Au-nanoparticle loaded ZnO NRs grown on glass substrate using hydrothermal technique. Scanning electron microscopy (SEM) shows that a thin ZnO seed layer on glass substrate plays a crucial role by providing effective nucleation centres for vertically aligned growth of ZnO NRs on the glass substrates. Optical characterization performed by UV-VIS-NIR spectroscopy shows that absorption characteristics of such an ensemble of ZnO NRs can be enhanced significantly by loading the NRs with Au nanoparticles. To further understand enhancement and tunability of absorption characteristics of such arrays, finite-difference-time domain (FDTD) based numerical analysis has been performed taking into account plasmonic effects. The results of our analysis show that the absorption edge, transmittance and resonant peaks of such arrays can be significantly controlled by varying the NR diameter, gap, Au-

particle size and NR density of the array. Such characteristics are promising for designing and realizing a variety of photonic and optoelectronic devices employing the low-cost deposition technique of hydrothermal processing.

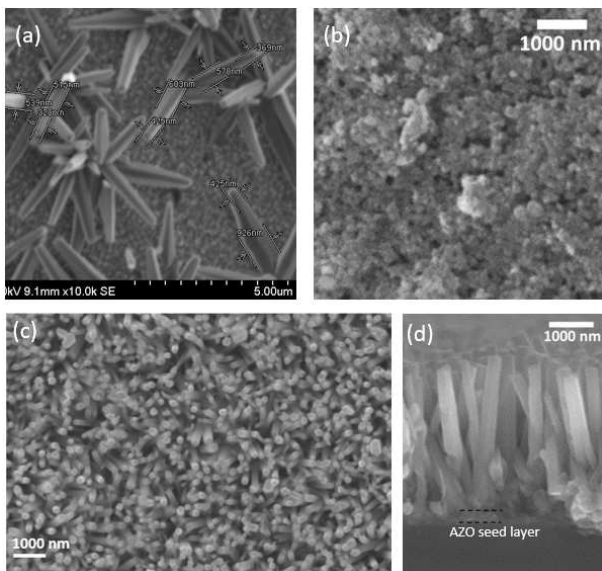


Figure 1: SEM images of (a) ZnO nanorods grown on Fluorine doped tin oxide (FTO) substrate without ZnO seed layer, (b) Al-doped ZnO (AZO) seed layer on glass substrate, (c) Plane-view of ZnO nanorods grown on AZO seeded glass substrate and, (d) cross-sectional view of ZnO nanorods grown on AZO seeded glass substrate (AZO seed layer marked by dashed black lines in the image)

## II. EXPERIMENTAL METHODS

### A. Material Growth and Deposition

The ZnO NRs studied in this work were synthesized on sol-gel spin coated ZnO seed-layers [2] which acts as a nucleation centre for subsequent growth of NRs grown by hydrothermal process. Different techniques, such as pulsed laser deposition, spray pyrolysis, atomic layer deposition, sol-gel technique, SILAR, metal organic chemical vapour deposition and thermal decomposition of drop-casted Zn acetate solution [1, 2, 14], have been reported for the growth of such seed layers. The present study utilized the sol-gel derived technique, which is relatively cost-effective, environment friendly and easy to implement. Prior to seed layer deposition, substrates were cleaned by ultra-sonication in acetone, isopropanol and DI water. To grow the Al-doped ZnO (AZO) seed layer, Zinc acetate dehydrate and Aluminium chloride hexa-hydrate was mixed into absolute ethanol to get molar ratio [Al/Zn] of the dopant of 0-3 at %. This solution was then spin-coated onto the substrate of interest and the seed layer thickness was increased by repeating the coating process several times [2]. The seeded substrate was then annealed for 1 hour at 250 °C with a temperature rise of 5 °C/min and then cooled down to room temperature.

Hydrothermal growth of ZnO NRs atop the seeded substrate was performed using zinc nitrate hexahydrate (ZNH) and hexamethylenetetramine (HMT). It is to be noted that to observe the effect of seed layer on ZnO NR growth, a test sample atop the FTO substrate without ZnO seed layer was also grown using hydrothermal technique [15]. Aqueous solutions of ZNH and HMT were prepared separately and then mixed to form the liquid precursor. The ZnO- or AZO- seeded

substrate was subsequently put inside this solution, which was heated up to about 90 °C in a thermostatically controlled oil bath for over 80 minutes. During this time, the solution changed color from clear to cloudy, confirming the reaction

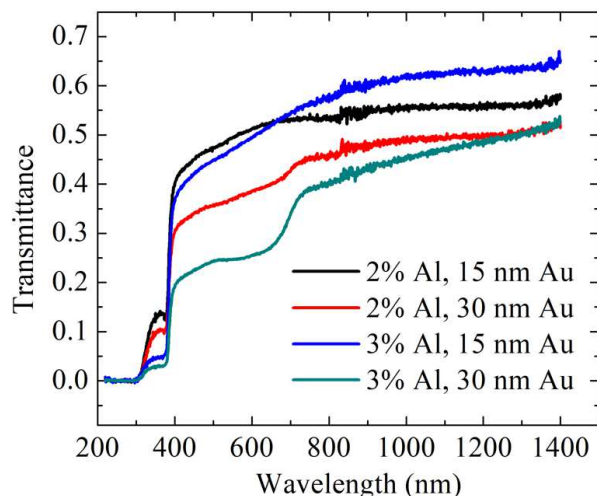


Figure 2: Measured transmittance of Au-nanoparticle loaded ZnO nanorod samples grown with AZO seed layers of two different Al-compositions (2% and 3% Al respectively); the effect of two different diameters (15 nm and 30 nm) of gold nanoparticles has been shown herein

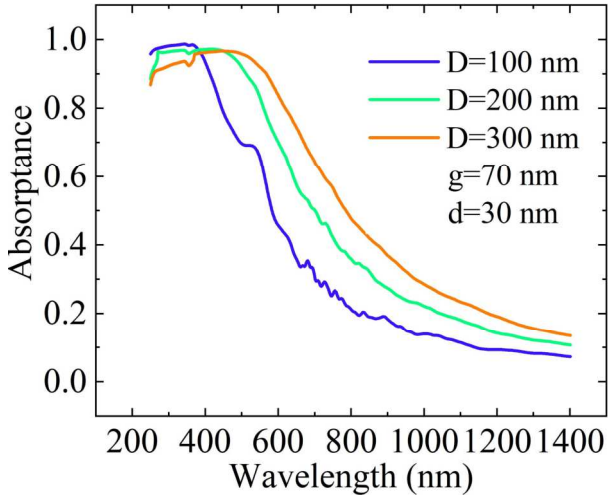
and deposition onto the substrate. About 90 min after the end of deposition, the substrate was removed from the solution and rinsed with DI water and dried under hot air flow. To remove any organic deposits coming from the bath solution, this hydrothermally grown thin film was given the same post-heat treatments that of seeding layer, i.e. 1 hour annealing at 250 °C. Finally, the ZnO NRs on AZO (Al:2%, 3%) seed layers were loaded with ~20-30  $\mu$ L colloidal gold (Au) solutions (particle size 15 nm and 30 nm from Sigma-Aldrich) for investigating their effects on the optical properties of aligned ZnO NRs.

### B. Experimental Characterization

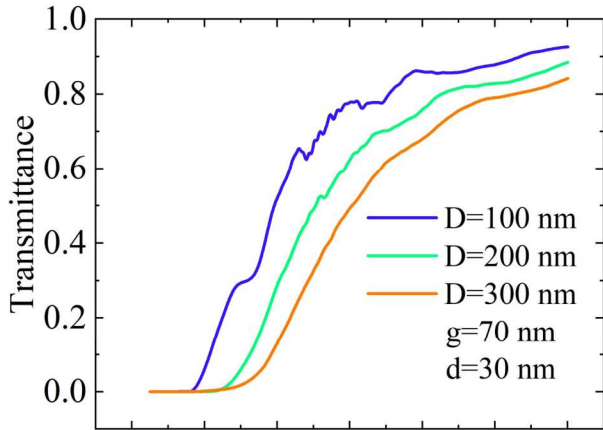
Surface morphology of the as-grown and -deposited materials were studied by scanning electron microscopy (SEM). In Fig. 1(a), an SEM image of ZnO NRs grown on non-seeded FTO substrate is shown. As can be observed, without seed layer the NRs appear to be dispersed and misaligned with respect to each other. Also diameters of the NRs appear to vary over a wide range of ~ 300-950 nm. An SEM image of the Al-doped ZnO seed layer on normal microscopy glass slide, grown prior to NR growth, is shown in Fig. 1(b). Such seed layers, having grain size of about 50 nm, serve as nucleation centres for NR growth. It is noteworthy that over a reasonably large area of ~ 40  $\mu$ m  $\times$  30 $\mu$ m, the optimized seed layer surface was found to be free from any micro-cracks and pinholes. Such characteristics are conducive for the subsequent growth of nanostructures, and also for micrometer scale (opto)electronic devices [15].

The SEM image of an array of ZnO NRs grown on AZO seed layer is shown in Fig. 1(c). These NRs are observed to have well-defined hexagonal facets, therefore suggesting *c*-axis growth. The NR density of this array is measured to be  $\sim(1.50 \pm 0.25) \times 10^9$  per  $\text{cm}^2$  and they are found to be nearly vertically aligned with the glass-substrate. From cross-sectional SEM imaging of the same sample (shown in Fig. 1(d)), the thickness of the AZO seed layer beneath the NRs is

calculated to be  $\sim 232 \pm 34$  nm and lengths of the NRs are estimated to be between 1.5 - 3  $\mu\text{m}$  depending on deposition time. These results confirm the beneficial role of the seed layer, which has promoted the growth of well-aligned nanorods. As can be observed from Fig. 1(a), the non-seeded NRs are rather randomly oriented along arbitrary directions with lengths extending up to about 10  $\mu\text{m}$ .



(a)



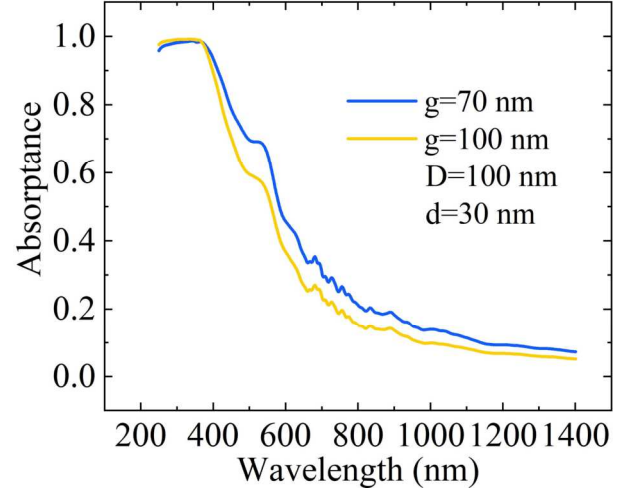
(b)

Figure 3: Effect of NR diameter variation on (a) absorption and (b) transmission characteristics of periodically arranged NR array having spacing of  $g = 70$  nm and gold nanoparticle diameter of  $d = 30$  nm

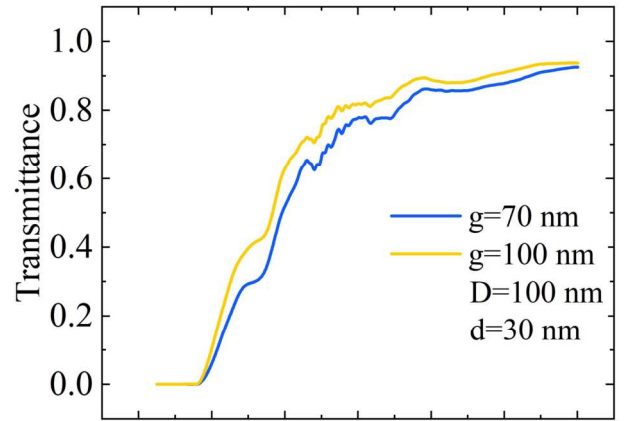
For optical characterization of the Au-loaded ZnO NRs, transmission characteristics were measured at room temperature. These measurements were performed with a UV-VIS-NIR spectrometer coupled with an integrating sphere. A custom made black mask with a mm-scale hole was used during this measurement to ensure that illumination area of all samples being investigated remained the same. The measured transmittance spectra, obtained after baseline correction and normalization by the incident optical flux, are shown in Fig. 2. Samples having two different compositions of Al-doped ZnO were considered during these measurements. Furthermore, the effect of metallic nanoparticle size on optical characteristics are also investigated by measuring transmittance of samples having Au-particles of 15 nm and 30 nm in diameter.

### III. SIMULATION AND ANALYSIS

The experimental results of Fig. 2 show that the size of Au-nanoparticles has significant impact on the transmission characteristics of the ZnO NRs. To understand the experimental results and also to predict tunability of the absorption characteristics, finite difference time domain (FDTD) simulation has been performed taking into account



(a)

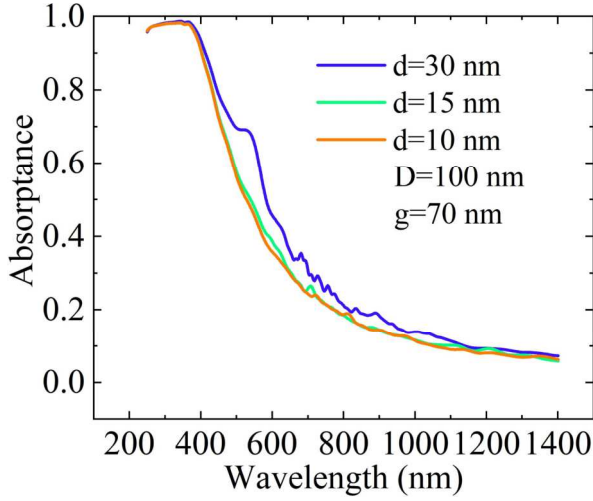


(b)

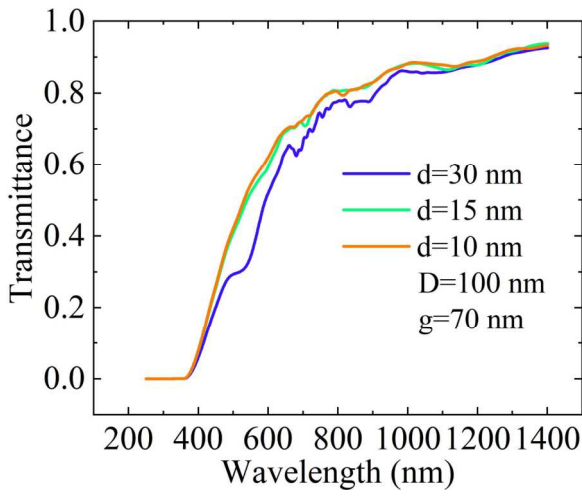
Figure 4: Effect of NR-to-NR spacing variation on (a) absorption and (b) transmission characteristics of periodic NR arrays having NR diameter of  $D = 100$  nm and Au-nanoparticle diameter of  $d = 30$  nm

appropriate boundary conditions. For simplicity of analysis and also to reduce computational burden, a periodic array of ZnO NRs has been considered in this work. The three-dimensional (3D) numerical analysis of this work considered a fixed height of 1.8  $\mu\text{m}$  of the NRs in accordance with the results of SEM imaging. Refractive index values of ZnO NRs, AZO and glass substrate have been modelled based on experimental results reported in [16-18]. In accordance with the optical measurements of this work, normal incidence of a broadband light has been considered throughout the study to calculate the transmission and absorption characteristics of the NR array.

To understand the effect of lateral dimension of the NRs on overall absorption characteristics of the array, NR diameter ( $D$ ) has been varied from 100 - 300 nm while keeping Au-particle diameter ( $d$ ) and NR-to-NR gap ( $g$ ) constant at 30 nm and 70 nm respectively. It may be noted that these dimensions



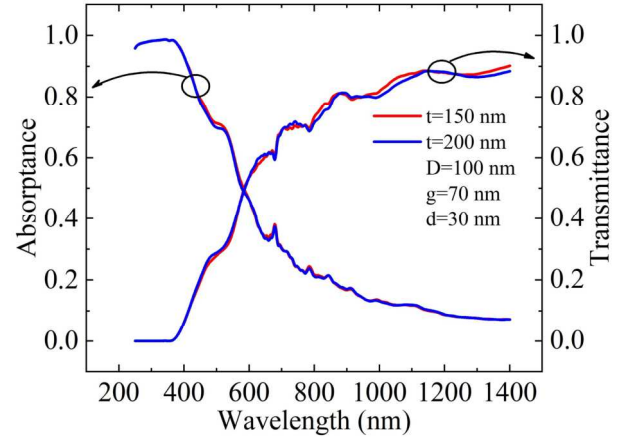
(a)



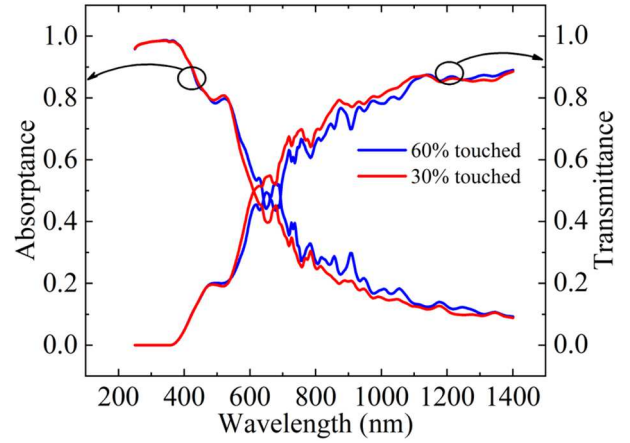
(b)

Figure 5: Effect of Au-nanoparticle diameter variation on (a) absorption and (b) transmission characteristics of periodically arranged NR arrays having spacing of nanorod diameter,  $D = 100$  nm and NR-to-NR spacing  $g = 70$  nm

correspond to an areal density between  $\sim(1.5 \times 10^9$  per  $\text{cm}^2$  to  $0.75 \times 10^9$  per  $\text{cm}^2$  which is around the range obtained from SEM imaging in this study. As shown in Fig. 3, absorption increases and consequently transmittance decreases with increasing diameter of the NRs. Furthermore, the absorption peak tends to right-shift because of resonance effects resulting from multiple-scattering of light in the NR-array [19-21]. Such absorption enhancement and consequent decrease of transmittance at longer wavelengths can be explained in terms of NR filling-fraction ( $f$ ) as well, which is defined as,  $f = \frac{\pi D^2}{4a^2}$ , where  $a=D+g$ . Increasing the NR diameter while keeping the distance between the NRs constant increases  $f$  (i.e. areal density of the NRs) and therefore increases effective refractive index ( $n_{\text{eff}}$ ) of the composite medium. As has been shown in previous analysis based on effective medium theory, such increase of  $n_{\text{eff}}$  causes the resonant peak of absorption spectra to red-shift in such systems of dielectric absorbing medium [19]. Here it is important to note that from a practical standpoint, fill-factor of the array cannot be increased arbitrarily if high-quality growth of the NRs is to be maintained. Furthermore, it has also been shown that as the areal density of NRs tend to approach very high values, the



(a)



(b)

Figure 6: (a) Effect of AZO seed layer thickness variation on absorption and transmission of periodically arranged NR arrays having nanorod diameter of  $D = 100$  nm, NR-to-NR spacing of  $70$  nm and Au-particle diameter of  $30$  nm; (b) absorption and transmittance spectra obtained for the cases when 30% and 60% of the Au-particles are touching the AZO seed layer

material tends to behave more like a bulk, and consequently peak-absorption value decrease because of the loss of resonant characteristics at the wavelengths of interest [19].

As the fill-factor of the NR assembly increases with decreasing gap between the NRs (while keeping  $D$  constant), the absorption of the array also increases (Fig. 4(a)). As a result, the transmission decreases with decreasing NR-to-NR distance in the array (Fig. 4(b)). Therefore, for a fixed dimension of the NRs, high areal density is considered to be favourable for absorption enhancement- provided that such density permits high quality growth. The effect of Au-nanoparticle size variation on absorption and transmittance are shown in Fig. 5. In accordance with experimental results, transmittance tends to decrease with increasing diameter of Au-particles. This decrease is related to the absorption enhancement resulting from enhanced plasmonic effect in the array. The absorption enhancement is especially prominent at around  $550$  nm, which is confirmed as the surface plasmon resonance peak both in simulations and experiments. It is to be noted that the plasmonic resonant peak of commercially available spherical Au-nanoparticles varies from  $520$ - $570$  nm as the nanoparticle size varies from  $20$ - $100$  nm [22]. Therefore, the observed simulation and experimental results

are very well within reported values of plasmonic resonance. The plasmonic resonant peaks of such Au-loaded ZnO NRs may possibly be extended into the near-infra-red regime as well by loading commercially available nanoparticles of other shapes, such as urchins or nanostars [22].

Finally, to understand the effect of AZO layer thickness, transmittance and absorption are calculated for two different thicknesses ( $t$ ) of AZO. As can be observed, thickness variation of the AZO layer has negligible effect on absorption and transmittance characteristics of the NRs. Therefore, the contribution of AZO is mainly morphological, i.e. though it enables vertically oriented growth of NRs, it does not itself enhance optical absorption. However, because AZO is highly conducting, it may indeed influence plasmonic resonance of Au-nanoparticles depending on whether it is touching the nanoparticles or not. To examine this effect, two different cases of Au-nanoparticle loaded ZnO NRs have been considered, in which 30% and 60% of the Au-nanoparticles are in contact with the AZO layer. The results are shown in Fig. 6(b) which suggests that the AZO layer in fact influences the plasmonic resonant peaks to some extent. Such interaction should be stronger for higher density and larger size of the metallic nanoparticles, and also possibly for higher mole fraction of Al-content in the AZO layer. These aspects were beyond the scope of the present work and are prospective areas of investigation in future research.

#### IV. CONCLUSION

In summary, light absorption and transmission characteristics of hydrothermally grown Au-nanoparticle loaded ZnO nanorods have been investigated based on experiments and FDTD simulations. Materials growth and scanning electron microscopy imaging show that the presence of a seed layer significantly facilitates the growth of nearly vertically oriented Au-nanoparticle loaded ZnO nanorods on a glass substrate. Optical measurements confirm absorption enhancement of such arrays because of plasmonic effects resulting from the gold nanoparticles. The experimental results are supported well by numerical results obtained from FDTD simulations of the three-dimensional photonic structure. The simulation results also show that absorption profile of such arrays can be appreciably tuned from visible to near-infra-red region of the electromagnetic spectrum by controlling diameter and areal density of the nanorods. By controlling size and density of the metallic nanoparticles, tunability is obtained primarily in the vicinity of the plasmonic resonant peak. The present study also suggests scope of future research, such as further tuning of the absorption and transmission characteristics by incorporating metallic nanoparticles of different shapes and sizes, and also by tailoring the plasmonic interaction between the Au-nanoparticles and the highly conducting Al-doped ZnO layer underneath.

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#### REFERENCES

[1] Ghos BC, Farhad SF, Patwary MA, Majumder S, Hossain MA, Tanvir NI, Rahman MA, Tanaka T, Guo Q. Influence of the Substrate, Process

Conditions, and Postannealing Temperature on the Properties of ZnO Thin Films Grown by the Successive Ionic Layer Adsorption and Reaction Method. *ACS omega*. 2021 Jan 21;6(4):2665-74.

[2] Farhad SF, Tanvir NI, Bashar MS, Sultana M. Synthesis and characterization of c-axis oriented Zinc Oxide thin film and its use for the subsequent hydrothermal growth of Zinc Oxide nanorods. *MRS Advances*. 2019;4(16):921-8.

[3] Hiramatsu M, Imaeda K, Horio N, Nawata M. Transparent conducting ZnO thin films prepared by XeCl excimer laser ablation. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*. 1998 Mar;16(2):669-73.

[4] Nayeri FD, Soleimani EA, Salehi F. Synthesis and characterization of ZnO nanowires grown on different seed layers: the application for dye-sensitized solar cells. *Renewable Energy*. 2013 Dec 1;60:246-55.

[5] Xu J, Chen Z, Zapfen JA, Lee CS, Zhang W. Surface engineering of ZnO nanostructures for semiconductor-sensitized solar cells. *Advanced Materials*. 2014 Aug;26(31):5337-67.

[6] Zhang Z, Liao Q, Yu Y, Wang X, Zhang Y. Enhanced photoresponse of ZnO nanorods-based self-powered photodetector by piezotronic interface engineering. *Nano Energy*. 2014 Oct 1;9:237-44.

[7] Greene LE, Law M, Tan DH, Montano M, Goldberger J, Somorjai G, Yang P. General route to vertical ZnO nanowire arrays using textured ZnO seeds. *Nano letters*. 2005 Jul 13;5(7):1231-6.

[8] Schmidt-Mende L, MacManus-Driscoll JL. ZnO-nanostructures, defects, and devices. *Materials today*. 2007 May 1;10(5):40-8.

[9] Vayssieres L. Growth of arrayed nanorods and nanowires of ZnO from aqueous solutions. *Advanced Materials*. 2003 Mar 4;15(5):464-6.

[10] Farhad SF. The effect of substrate temperature and oxygen partial pressure on the properties of nanocrystalline copper oxide thin films grown by pulsed laser deposition. *Data in Brief*. 2021 Feb 1;34:106644.

[11] Majumder S, Tanvir NI, Ghos BC, Patwary MA, Rahman MA, Hossain MA, Farhad SF. Optimization of the growth conditions of Cu<sub>2</sub>O thin films and subsequent fabrication of Cu<sub>2</sub>O/ZnO heterojunction by m-SILAR method. In 2020 IEEE International Women in Engineering (WIE) Conference on Electrical and Computer Engineering (WIECON-ECE) 2020 Dec 26 (pp. 139-142). IEEE.

[12] Cheng B, Samulski ET. Hydrothermal synthesis of one-dimensional ZnO nanostructures with different aspect ratios. *Chemical Communications*. 2004(8):986-7.

[13] Laudise RA, Ballman AA. Hydrothermal synthesis of zinc oxide and zinc sulfide. *The Journal of Physical Chemistry*. 1960 May;64(5):688-91.

[14] Islam MR, Rahman M, Farhad SF, Podder J. Structural, optical and photocatalysis properties of sol-gel deposited Al-doped ZnO thin films. *Surfaces and Interfaces*. 2019 Sep 1;16:120-6.

[15] Farhad SF, Tanvir NI, Bashar MS, Hossain MS, Sultana M, Khatun N. Facile synthesis of oriented zinc oxide seed layer for the hydrothermal growth of zinc oxide nanorods. *Bangladesh Journal of Scientific and Industrial Research*. 2018 Dec 9;53(4):233-44.

[16] Rubin M. Optical properties of soda lime silica glasses. *Solar energy materials*. 1985 Sep 1;12(4):275-88.

[17] Ting CC. Structure, morphology, and optical properties of the compact, vertically-aligned ZnO nanorod thin films by the solution-growth technique. InTech: Shanghai, China; 2012 Mar 9.

[18] Treharne RE, Seymour-Pierce A, Durose K, Hutchings K, Roncallo S, Lane D. Optical design and fabrication of fully sputtered CdTe/CdS solar cells. In *Journal of Physics: Conference Series* 2011 Mar 1 (Vol. 286, No. 1, p. 012038). IOP Publishing.

[19] Zaman S, Hassan MM, Hasanuzzaman M, Baten MZ. Coscinodiscus diatom inspired bi-layered photonic structures with near-perfect absorptance accompanied by tunable absorption characteristics. *Optics Express*. 2020 Aug 17;28(17):25007-21.

[20] Yang B, Feng P, Kumar A, Katiyar RS, Achermann M. Structural and optical properties of N-doped ZnO nanorod arrays. *Journal of Physics D: Applied Physics*. 2009 Sep 14;42(19):195402.

[21] Lee HK, Kim MS, Yu JS. Effect of AZO seed layer on electrochemical growth and optical properties of ZnO nanorod arrays on ITO glass. *Nanotechnology*. 2011 Oct 7;22(44):445602.

[22] Cytodiagnosics Inc. 2021. *Gold Nanoparticle Properties*. [online] Available at: <<https://www.cytodiagnosics.com/pages/gold-nanoparticle-properties>> (Accessed on: 19 October, 2021).