Plasmonic Effect of Metal Nanoparticles Deposited on Wide-Band Gap Metal Oxide Nanowire Substrate

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<td>ALD</td>
<td>Atomic Layer Deposition</td>
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<td>Aluminium oxide</td>
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<td>Au</td>
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<td>Cu</td>
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<td>DSSC</td>
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<td>TiO$_2$</td>
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Abstract

The application of nanowires (NWs) in solar cells (SCs) is of great interest due to their new promising aspects established in nanoelectronics. Semiconductors associated with plasmonic metal nanoparticles (NPs) such as Silver (Ag), Gold (Au) and Copper (Cu), show enhanced performance in solid state light absorbing SCs owing to plasmonic characteristic of noble metal NPs.

Plasmonic NPs presented a significant role in development of visible light harvesting for many applications such as photocatalytic materials, photodynamic in Surface Enhanced Raman Spectroscopy (SERS) and photovoltaics (PVs). Integration of plasmonic NPs in semiconductor materials have opened the routes to expand new PV systems with high efficiency light absorption. In this project, we introduce the synthesis ZnO and TiO2 NWs used as N-type semiconducting substrates and various methods for isolating plasmonic metal NPs, which are later deposited on the semiconducting substrates.

Vertically aligned ZnO and TiO2 NWs arrays were grown on the fluorine-doped tin oxide (FTO) conductive glass substrates via hydrothermal method at low temperature and the plasmonic NPs were synthesized by wet chemistry procedures and finally decorated on the NW films by using electrophoretic deposition.

The impact of metal NPs loaded on the ZnO and TiO2 NWs substrates was studied by means of UV-vis spectroscopy and Photoluminescence (PL) spectroscopy. The absorbance spectra of individual NPs were recorded. Remarkably, the reflectance spectra of produced samples presented an enhancement in light absorption of the substrates after uptake of NPs on the ZnO and TiO2 NWs. The optical properties of the as grown ZnO NWs films decorated with Ag NPs (I) in direct contact with substrate and (II) in presence of an Al2O3 insulating spacer layer have been investigated. Both systems exhibited an enhancement in the UV band-edge emission from the ZnO when excited at 325 nm. In contrast, the broad bend defect emission of the samples did not have a significant change compare to bare ZnO substrates.

The observed results suggested that the ZnO and TiO2 NWs decorated with plasmonic nanoparticles can boost the optical properties of MOs NWs substrates and hence effectively enhance the separation of photoexcited electron-hole pairs and photo-conversion applications.
1. Introduction

Nowadays, the increasing demand for energy consumption and on the other hand the shortage of the fossil fuels in the world has forced researchers to look for renewable power sources and other sustainable types of energies. Solar radiation with the abundant energy flux intercepted by earth (~ 6.26×10²⁰ J/h), [1,2] is believed to be one of the primary sources of renewable energy and an alternative to the traditional types of energy. Typically, there are two common types of solar energy systems used to convert the solar radiation into useful heat or electricity. Photovoltaics (PV) and Thermal systems. Several researches have been conducted on the photovoltaic (PV) devices capable of converting the sun light into electrical energy. PV solar cell (SC) is basically a semiconductor diode that absorbs the incoming photons of light and creates electron-hole pairs [3].

PV solar cells for energy generation also have their advantages and limitations based on their operation principle, physical efficiency and fabrication technologies. The main route currently used and emphasized in the PV fabrication industries is silicon based solar cells. Crystalline wafer based silicon solar cells manufactured by the Czochralski method are the most dominant in terms of production [4]. however, cost of silicon accounts for over 50% of the total contribution to the production price of the crystalline silicon solar cells, [5] which is considered one of the main drawbacks of these PV systems. To make silicon cells more cost efficient, several strategies have been proposed including reduction of the silicon wafer thickness by different sawing techniques and depositing hydrogenated amorphous silicon as a thin film solar cell [6].

Despite the tremendous progress in all aspects of production of Si based solar cells and rapid drop of their production cost for PV systems, yet their low carrier mobility in amorphous state, poor optical transparency, lower mechanical flexibility of their final PV cells, and high energy consumption of their manufacturing techniques (high temperature deposition), present challenges for their further development [4,7]. Some of these limitations have caused researchers to explore different types of semiconducting materials as a replacement for the silicon based solar cells (SCs).

A comparative study is done for different semiconducting materials used in PV systems, based on their cell structure, production method, durability and price variation. Semiconductor materials used in SCs are usually divided into three categories. The first-generation SCs that are relatively expensive to produce and have low efficiency. The second generation contains types of SCs that have even lower efficiency but are much cheaper to produce (lower temperature and lower cost) [8]. The term third generation SCs are used for the new promising technologies that are more efficient but are not yet available in the market. Some of the most developed third generation SCs are as follows [9]:

1. Nano crystal based SCs
2. Polymer based SCs
3. Dye sensitized SCs
4. Solar concentrators
There has been enormous research in nanocrystal based SC’s functioning in PV systems. Specific physical and chemical properties of nanostructured materials including their size, shape, surface area, surface porosity, reactivity and optoelectrical properties makes them suitable candidates for several applications such as PV systems. The significant properties of nanomaterials that can be tailored to their controllable size and shape makes them of both basic and practical interests leading to novel applications. For instance, nanostructures made of well-aligned nanowires or nanorods of semiconducting metal oxides (MOs), exhibit fast and effective transport of electrons along with effective scattering of light in the solar spectrum [8].

1.1 Wide band gap semiconducting-nanostructured Metal Oxides (MOs)

The variety of electronic and chemical properties of MOs with wide optical band gap makes them exciting materials for technological applications. MOs are one of the most abundant materials in the earth crust. Furthermore, MOs nanostructures, exhibit unique properties including excellent carrier mobility, high optical transparency, non-toxicity and long term stability, which offers the possibility of constructing high quality and long lasting PV systems [7]. In our current work, we mainly focus on development of ZnO and TiO$_2$ NWs that are potentially known metallic semiconductors and widely used in various applications such as photocatalysis and PV systems.

1.2 MOs nanowires

MOs nanowires are unique 1D nanostructures with wide range of applications in optoelectrical, chemical, photodetectors, gas sensors, wave guides and semiconductor technologies [10]. Significant number of advanced methods on growth of various 1D nanostructures of MOs have been reported, where desired heterojunctions and compositions can be feasibly synthesized. So far various MOs NWs semiconductors such as CuO [11,12], TiO$_2$ [13,14], Al$_2$O$_3$ [15,16], MgO [17] and ZnO [18,19] have been employed for optoelectronic applications in SCs and PV technologies. Several methods have been developed to synthesize 1D MOs nanostructures including vapor solid-phase technique [12,15,17], chemical solution deposition (sol-gel) [13,20], template etching [16], precipitation [18], micro emulsion [21], flux growth [22] and hydrothermal method. The nanostructures made of these materials represent a new class of semiconductors suitable for light absorbing, light amplification and light detection applications. A fully integrated sub structure of MOs NWs has shown great functionalities at many technological dimensions specifically SCs technologies. In this work, we mainly investigate on the substructures fabricated from ZnO and TiO$_2$ NWs via hydrothermal method. A general description about ZnO and TiO$_2$ NWs and their physical and chemical properties as anode in thin film SCs is presented below.

1.2.1. ZnO NWs

Over the last decade, considerable attention has been devoted to the investigation of direct wide band gap semiconductors owing to their unique optical and electrical properties [60]. Zinc oxide (ZnO) with band gap of ~3.37 eV and exciton binding energy of ~60 meV is one of the most studied wide band gap semiconductors for optoelectrical applications [23]. Furthermore, ZnO nanowires (NWs) are of crucial importance in sub-wave length electron guides due to their well-defined transition dipoles and highly crystalline structure. On the other hand, their uncontrolled conductivity (compared with indirect band gap crystalline semiconductor
materials) and their lattice imperfections resulted from native and intrinsic defects, limits their performance in many optical fields like photovoltaic cells [25].

ZnO initially was considered as a suitable substrate for other nanostructure alloys like GaN [24]. However, its high quality of bulk crystals and strong luminescence in the UV region have caused numerous researches over this material [25]. ZnO nanomaterials have been reported in various forms such as nanohelices, nanocolumns, nanotubes, nanorods, nanowires, nanorings, nanobelts, and nanocrystals and as a wide range of porous materials in ceramics [26]. ZnO NWs is the only structure studied by this work among other configurations of this material. The main crystal habit reported for this nanostructure was the Wurtzite formation with hexagonal cross section as shown in Figure 1.

Figure 1: Wurtzite structure of single nanowire of ZnO [27]

Vapor-phase technique, pulsed laser deposition (PLD), electrochemical deposition and hydrothermal synthesis method are the most dominant techniques for synthesis of ZnO NWs [27]. ZnO NWs synthesized in this project were also fabricated using hydrothermal method due to the lower temperature and simplicity of this method.

Various experimental measurements have been conducted on different ZnO structures in SCs and PVs. At early stages, ZnO NWs were introduced in Dye Sensitized Solar Cells (DSSC) which caused a considerable improvement in electron transport and red shift band of DSSCs [28]. Other literature reported a lower fill factor in N3 DSSCs by using the ZnO NWs [29]. Different type of thin film SCs have also been fabricated by other groups with depositing P-type Cu2O on the ZnO nano arrays, however the efficiency was not comparable with corresponding DSSCs with ZnO NWs (4.17%) [30]. Vertically aligned ZnO NW substrates, deposited with Gold Nanoparticles (Au NPs) were also studied. Results showed that the NPs enhanced the optical absorption of the ZnO NWs by Surface Plasmon Resonance (SPR) and at the same time increase the charge separation in ZnO conduction band [31].

Despite the number of advantages obtained by using ZnO for optoelectrical applications, controlling over the conductivity and intrinsic defects carried out by their synthesis method remains a challenge. Consequently, several investigations have focused their work on
optimizing the optoelectrical properties of ZnO NWs by several methods such as grafting the ZnO NWs with other photoanodes like TiO$_2$ or coating NWs by different plasmonic NPs like Ag NPs or Au NPs [31,32,33].

This project also remarks the methods for increasing the efficiency of ZnO and TiO$_2$ substrates by embedding different plasmonic metallic NPs on the NWs substrates. In the experimental section of this report the selected method for growth of ZnO NWs in our work is also explained further in details.

### 1.2.2. TiO$_2$ NWs

TiO$_2$ NWs has been extensively used for photocatalytic, electrochemical and PV systems due to merits of their nontoxicity, chemical stability and cheap production cost [34]. TiO$_2$ has numerous applications in pigments, self-cleaning coatings, sun screens, water splitting and PVs. In addition, TiO$_2$ nanostructures including nanoparticles, nanorods, nanowires and nanotubes are widely used in gas sensors, DSSCs, PVs and electronic applications [35].

A series of pathways for synthesis of TiO$_2$ nanostructures is documented, including sol-gel method, solvothermal method, direct oxidization, chemical vapor deposition (CVD) and hydrothermal method [35]. In this project, we also simply demonstrate a facile synthesis method of TiO$_2$ NWs via hydrothermal method.

Basically, TiO$_2$ in the bulk state is a wide band gap n-type semiconductor (3.2 eV). Nanoscale forms of TiO$_2$ are of importance because they offer high surface area and more reactivity sites. The implementation of this kind of NWs in the DSSCs, has a reported efficiency of 10% [36]. Even though TiO$_2$ nanoparticles present superior properties in providing a large surface area, however existence of numerous interfaces and intrinsic defects in their nanostructure is regarded as an unfavorable factor that may increase the electron-hole recombination and reduce the efficiency of final structure. Doping the TiO$_2$ NWs with metals and metal NPs is an effective way to lower the band gap of the TiO$_2$ NWs and increase their photocatalytic efficiency. As an example, doping the TiO$_2$ NW films with Cu$^{2+}$ NPs is reported to enhance the photodegradation ability of the mentioned films by 40% compared to unmodified films [37]. Pu et al reported a photoactivity enhancement of Au–decorated TiO$_2$ NWs in the entire UV-vis region from 300nm to 800nm by using different shapes of Au NPs [38]. The plasmonic effect of Ag NPs and Au NPs decorated on the TiO$_2$ NWs DSSC is also investigated. Obtained results presented an efficiency enhancement of 21.6% for TiO$_2$-Au NPs and 27% for the TiO$_2$-Ag NPs [39].

### 1.3 Thin film solar cells

The definition of thin film solar cells is best remarked by Chopra et al [40]. Thin film SCs in PV technologies is defined as film of material created by nucleation and growth of molecular species on a substrate. Thin films SCs may possess different thickness varying from a few nanometers to tens of microns. The typical thickness of Semiconductors used in PV systems was between 1-3 microns. Basically, the main principle behind the thin film SCs is to reduce the travelling distance for the photo generated electrons and holes inside the cell to cell contacts and consequently increase the produced power. This type of behavior, reduces the demand for high crystallinity, high temperature and final cost of the produced SCs. The dominant structure
for thin film SCs is to create P-N junction by using different layers. Cu(In,Ga)Se$_2$, CdTe are some of the most typical industrial made thin film solar cells [40].

In this project, we mainly focus on the fabrication of a suitable structure for a metal oxide based substrate to be used in thin film SCs by incorporating ZnO and TiO$_2$ NWs as N-type MOs semiconductor. However, in order to promote the light harvesting and engineering the band gap of NWs, metallic NPs is also deposited on the NWs. The properties and effect of plasmonic particles is further explained in the next section.

1.4 Plasmonic Effect General Mechanism
The free electrons in conduction band in some of the noble metals like Au and Ag are able to move through the materials bulk. However, the mean free path of electrons in the material’s molecules is actually way smaller than their bulk (for example for Au~50nm). Therefore, when free electrons of these metals with smaller dimensions (nanometer scale), couple with electromagnetic waves of incident light, start to oscillate collectively on the surface of metal NPs. This phenomenon, which occurs in the metal- dielectric medium interface is called Surface Plasmon Resonance (SPR). One of the typical behaviors that can be observed by plasmonic materials is called Localized Surface Plasmon Resonance (LSPR). As it is shown in Figure 2 LSPR takes place when metal NPs have smaller dimensions than the wavelength of incident light and it causes coherent oscillation of the electrons in conduction band. The plasmonic resonance can be simply detected by absorption or scattering spectroscopy and it is found to be altered by several parameters like shape, size and surrounding materials dielectric constant [41,42].

![Figure 2: Oscillation of the electrons in the conduction band of the metal NP by incident light with certain wavelength [43].](image)

Nowadays the interests in unique properties of plasmonic particles (mainly Au and Ag), have raised several investigations in different fields such as surface enhanced Raman spectroscopy, sensing technologies and PVs [44].

1.5 Size dependent properties of plasmonic particles
As it was mentioned before, one of the important factors affecting the plasmonic resonance of NPs was their size. The influence of gold nanoparticle size on the surface plasmon resonance is illustrated in Figure 3. Where the absorption maximum increases from 520 nm to 580 nm the gold nanoparticle size also varies from 9 nm to 100 nm for spherical NPs, respectively. UV-vis spectra were recorded for gold particles diluted in water.
1.6 Plasmonic induced resonance mechanisms in semiconductors

MOs thin film SCs exhibit many advantages in PV technologies such as their feasibility of manufacturing and lower production cost, compare to traditional SCs. However, in addition of their stability issues in some cases, their conversion efficiencies remain limited due to wide band gap of photo catalytic materials like ZnO and TiO\textsubscript{2}, recombination mechanisms and their heavier trapping behavior [43]. Several methods have been proposed to increase the efficiency issues in thin film SCs as mentioned before. Employing the plasmonic NPs on semiconductors is one of the most frequently investigated methods for improving the performance of MOs thin film SCs. The plasmonic NPs in PV systems present three pathways to enhance the efficiency of SCs. (I) light scattering, (II) hot electrons and (III) resonance energy transfer [45].

1.6.1 Scattering Mechanism

Scattering mechanism is one of the effective methods for improving the efficiency of SCs. Scattering cross section in plasmonic NPs is relatively higher than the normalized absorption cross section of incident light and can be increased by increasing the particles size and their distance from substrate. By reciprocity, increasing the scattering cross section can lead to much higher path length enhancement of SCs [46]. The effect of increasing cross sections in ZnO@Au@Cu\textsubscript{2}O nanostructures has been studied by Ren et al. The enhancement of photocatalytic effect under visible light and its relation to light trapping properties of NPs was investigated via experimental and simulation measurements [47]. The scattering cross section of the Ag and Au NPs on the Silicon substrates was modeled by Catchpole et al using the
Drude-Lorentz model. The results presented the relation between particle size and the distance of particles from substrate [46].

1.6.2 Plasmonic Hot Electrons
When metal NPs are exposed to the incident light, the oscillation of their electrons lead to (I) re-emission as scattering and (II) decohere oscillation into a hot electron distribution. The hot electrons have an energy equal or higher than the band gap energy of semiconductor. The high Fermi energy level of the hot electrons can overcome the electron-hole recombination in semiconductors and increase the photoconversion [45]. The effect of the hot electron process is recently studied in the core shell nanostructure of Ag@Cu2O. Consequently, the result exhibited larger red-shift band and photocatalytic activity by increasing the shell thickness [49].

1.6.3 Plasmon Induced Resonance Energy Transfer (PIRET)
In this case, the plasmonic NPs transfer the absorbed energy from metal to semiconductor via localized surface plasmon resonance (LSPR) and generate electron-hole pairs. In PIRET it is possible to invoke electron-hole pairs even below the band gap of the semiconductor. Unlike hot electron process, in PIRET there is no need for direct contact between metal NPs and semiconductor [48]. The effect of inserting an insulating spacer layer between core shell structures of Au@SiO2@Cu2O is investigated in previous literatures [45]. The main difference between hot electron transfer and PIRET is the direction of electron travel through metal NPs and semiconductor. As it is shown in Figure 4 unlike hot electron process, in PIRET the electrons are transferred from metal NPs to semiconductor.

![Figure 4: Schematic view of energy transfer between metal NPs and semiconductors via hot electron and PIRET mechanisms [48].](image)

In this project, we mainly focus on embedding Ag, Au and Cu NPs functioning as plasmonic nanocrystals on ZnO and TiO2 NWs semiconductors in order to investigate the plasmonic activity in the prepared PV systems and the governing mechanism of charge separation between metal NPs and semiconductors. So, in the next part we introduce the used metal NPs and we shortly review the previous work relevant to their application in PVs.
1.7 Ag NPs
Metallic nanoparticles (NP) have attracted a large number of research over the years and has grown into various fields of science. This is primarily due to number of advantageous properties that these materials present in many pathways. Among all, the fields of biomedical science, electrical and physical engineering are heavily influenced by these materials.

Silver nanoparticles (Ag NPs), have gained a substantial attention due to their unique features in electrical conductivity, surface plasmon and antimicrobial properties. Generally, Ag NPs can be synthesized by various developed methods, including chemical reduction, polyol process, thermal decomposition, laser ablation and in situ chemical synthetic method [50].

Ag NPs have previously used in photoactive materials (metal-semiconductor) and resulted in significant increase in photodegradation activity under visible light ([59]). The photocatalytic experiments of the nanocomposite deposited on an electrochemically active film showed a great photodegradation of methyl orange and methylene blue [59]. In another case, Ag NPs were also decorated on the ZnO NWs via ultra violet irradiation of Ag ions for surface-enhance Raman scattering applications [32].

In the present investigation, we prepared Ag NPs using polyol method. In our synthetic route, poly(-vinyl pyrrolidone) (PVP) is used both as capping agent and size determining agent. Ethylene glycol is also used as suitable solvent for microwave reactions. The details of Ag NPs preparation will be described further in the experimental section.

1.8 Au NPs
Au NPs are the most stable metal nanoparticles, and they present fascinating aspects such as their size-related electronic, magnetic and optical properties, biocompatible, non-cytotoxic properties, surface functionalization, and their applications to catalysis and biology [51]. Examples of wide spread synthesizing methods for preparing gold nanoparticles are organic phase method of Burst, Martin method and Turkevich process via citrate. The selected method in our work was based on synthesizing the gold nanoparticles in toluene by Burst method which will be further mentioned in the experimental section [52].

1.9 Cu NPs
Nanoparticles prepared from earth-abundant and inexpensive sources have attracted a significant attention because of their promising potential for replacing the noble and the rare metals. Copper (Cu) is one of the widely-used materials in the world due to its important role in several industries, particularly in the electrical field due to its low cost and abundance [53].

Cu NPs have been studied extensively because of their catalytic, optical and conducting properties originating from an extremely large surface area to volume ratio and quantum confinement effects. Unlike Ag and Au nanoparticles, in which free-electron behavior is due to their notable dielectric functions, Cu NPs plasmonic responses to UV-vis at around 600 nm is believed to be because of interband transitions between the valance and Fermi energy level of the copper [54]. On the other hand, this can be in principle responsible for the comparatively weaker resonance shift of the Cu NPs.
A few methods have been reported for synthesizing Cu NPs including electron beam synthesizing [55], wire explosion method [56], reduction of Cu I and Cu II salts [57] and polyol method [54,58]. One of the main issues related with synthesizing the Cu NPs, is found to be the easily oxidized nature of the copper, which is enhanced even more in the nanometric scale and urges the use of the stabilizer and capping agents for fabricating these nanoparticles.
2 Objectives

The photoconversion efficiency of MOs semiconductors like ZnO and TiO$_2$ is limited by their inability to absorb visible light due to their wide band gap. One of the main aims of this work is to experimentally investigate the effect of integrating plasmonic NPs in the MOs wide band gap semiconductors.

So, this work is based on depositing the plasmonic NPs on semiconductor MOs NWs (on FTO glass) in order to:

- Increase the light absorption via light scattering
- Improve the separation of photoexcited electron-hole pairs, via surface plasmon resonance and localized surface plasmon resonance.
- Reduce the electron-hole recombination
- Increase the efficiency of the final PV system by engineering the band gap of NWs in order to exploit different regions of solar spectrum.
3 Experimental
In this part of the report we present the synthesis methods employed for producing ZnO NWs and metal NPs used in the experimental work of this project and finally the deposition procedure for uptaking the NPs on the NWs substrates.

3.1 ZnO NWs preparation
The ZnO nanowire arrays were synthesized via hydrothermal method, which has been reported by other groups [62]. Firstly, zinc acetate dehydrate \([\text{Zn(CH}_3\text{COO)}_2\cdot 2\text{H}_2\text{O}]\) was dissolved in ethyl alcohol to form a \(1\times 10^{-2}\) M solution. Then the sol was spin-coated on a FTO glass substrate in 4 cycles at a spinning rate of 3000 rpm using an Ossila spin coater. After each coating cycles, the substrate was heated at 120 °C for 10 minutes. The as-prepared substrate was calcinated in a furnace at ambient atmosphere at 450 °C for 2 hours to obtain ZnO seed layer. Secondly, the prepared seed layer was immersed in an aqueous solution of \(1\times 10^{-2}\) M zinc nitrate \((\text{ZnNO}_3)\) and \(1\times 10^{-2}\) M of hexamethylene tetraamine (HMT) inside a Teflon autoclave at 95 °C for 3 hours in order to grow ZnO NWs on the Zinc oxide seed layer. In the final step, the produced nanowire substrates were removed from the autoclave and washed with distilled water. Figure 4 shows every step of preparation of ZnO NWs in a schematic view.

![Figure 5: Schematic view of preparation process of ZnO NWs.](image)

3.2 Ag NPs synthesis (Polyol Method)
A \(1\times 10^{-3}\) M poly(-vinyl-pyrroldione) (PVP) solution and \(1\times 10^{-2}\) M silver nitrate \((\text{AgNO}_3)\) solution in 20 ml ethylene glycol were prepared. In order to have better dilution of compounds the solutions were mixed separately (PVP in 15 ml ETG and AgNO\(_3\) in 5 ml ETG) at room temperature and later on mixed together. Subsequently, the reaction took place in the Flexi Wave SK-1 microwave oven in 500 W for 40 s of MW radiation and the set temperature was 220°C. However, the reaction temperature raised only up to 120 °C.
3.3 **Ag NPs synthesis (Reduction method)**

Synthesis of Ag NPs with this method, involved the reduction of a silver salt such as AgNO₃ with a reducing agent like NaBH₄ without the presence of a colloidal stabilizer such as PVP. In this case, prepared NWs functioning as reaction substrate were immersed in the solution of AgNO₃ and subsequently transferred into a solution of NaBH₄ solution. Consequently, Ag NPs emerge on the NWs.

\[
2\text{AgNO}_3 + 2\text{NaBH}_4 \rightarrow 2\text{Ag} + \text{H}_2 + \text{B}_2\text{H}_6 + 2\text{NaNO}_3
\]

3.4 **Au NPs synthesis (Two Phase Method Via Toluene)**

In a typical procedure of synthesizing gold nanoparticles with toluene, a 3×10⁻² M solution of tetrachloroaauric acid (H₄AuCl₄) in 10 ml of distilled water. At the same time a 5×10⁻² M Tetraoctyl ammonium bromide (C₁₈H₄₄BN) solution in 26 ml of toluene (organic phase) has been prepared. Subsequently the two solutions were mixed by vigorous stirring. Meanwhile, the two mixtures were being stirred, another aqueous mixture of 0.4 M sodium borohydride
(NaBH4) in 8.3 ml water was added dropwise over a period of 20 minutes to the mixing components. In the final step, the whole mixture was transferred to a separator funnel and washed with distilled water and later on the organic phase containing Au NP was collected at the bottom of the separator. The dark velvet color of the separated phase indicates the formation of Au nanoparticles in the final solution.

![Diagram of Au NPs synthesis process via Two Phase method with TOAB.](image)

**Figure 7:** Au NPs synthesis Process via Two Phase method with TOAB.

3.5 Cu NPs Synthesis (Polyol Method/Reverse Micelle)

The synthesis of Cu NPs with this method included the following steps. A solution of $1 \times 10^{-3}$ M Poly vinylpyrrolidone (PVP, MW = $10^4$) and $1 \times 10^{-2}$ M copper chloride (CuCl$_2$) in 20 ml N,N dimethyl formamide (DMF) was prepared. In this reaction DMF acts not only as the reaction medium but also as a strong reducing agent. First reduction process was carried out in a Flexi Wave SK-1 microwave oven at 700 W and 70°C. The synthesis of the Cu$^+$-PVP molecules was detected by change of the solutions color from light green to blaze yellow. After decreasing the temperature of the reacting solution from 70°C to 55°C, an excessive solution of NaBH$_4$ in ethanol (2ml) was introduced to the reaction container to complete the second reduction process. The dark red color of the solution indicates the presence of the Cu NPs.
Figure 8: Cu NPs synthesis Process via Polyol Method.

An optical presentation of the prepared nanoparticles of Ag, Au and Cu can be observed in the Figure 9.

Figure 9: Images of prepared NPs from left to right; Au NPs, Cu NPs and Ag NPs.

Optical characterization of the as-prepared NPs precursors was carried out by Cary 5000 UV-Vis spectrophotometer, during all steps of the reduction procedure, which will be further explained in the result and discussion part of this report.

3.6 Electrophoresis deposition of NPs on the NWs substrate
NPs were uptaken on the nanowires by electrophoresis method. The electrophoresis experimental setup was prepared using a potentiostat. NWs substrates were used as a cathode electrode and a steel made electrode is used as anode. Considered electric potential between the electrodes varied between 9V, 10V and 15V corresponding to the different used NPs which were diluted in different solvents. The electrodes were placed at 3 cm distance from each other.
and the electrophoresis solution was constantly being stirred. Figure 10 shows a schematic view of the electrophoresis setup for this experiment.

![Electrophoresis setup](image)

**Figure 10: Electrophoresis setup used for depositing NPs on the NWs substrates.**

One of the advantages associated with using electrophoresis method as a deposition technique, is that it enables to estimate the number of NPs deposited on the substrates. These estimations are carried out by using Beer-Lambert Law which will be further explained in Result and Discussion part of this report.

### 3.7 Optical view of produced samples

<table>
<thead>
<tr>
<th>ZnO/Ag NPs</th>
<th>ZnO/Au NPs</th>
<th>ZnO/Cu NPs</th>
<th>TiO$_2$/Ag NPs</th>
<th>TiO$_2$/Au NPs</th>
<th>TiO$_2$/Cu NPs</th>
</tr>
</thead>
</table>
4 Result and discussion

4.1 Analyzing the electrophoretic deposition of NPs on ZnO nanowires

As it was mentioned before electrophoresis method can also be used to estimate the concentration of nano particles on the NWs film. In this section, we present the carried out uptaking analysis of Ag NPs and Au NPs on the ZnO NWs.

4.1.1 Analyzing the electrophoretic deposition of Ag NPs on ZnO nanowires

The electrophoresis experimental setup was prepared using a potentiostat. The adjusted potential between the electrodes was 9 V and the Ag NPs were diluted in 86 ml ethanol as an electrolyte solvent ([Ag NPs] =6.74×10^{-4} M). So, due to beer-lambert relation shown in equation (1) the molar absorptivity coefficient of our solution is measured as 2805.637 L mol^{-1} cm^{-1}. The absorption spectra of the solution have been recorded in different time intervals in order to analyze the deposition of the Ag on the ZnO substrate. (Figure 11)

![Absorption spectra of the Ag NPs-ethanolic solution during the electrophoresis process.](image)

It can be seen that, by moving toward the electrophoresis process, the absorption intensity of the Ag NP/ethanol solution is slightly decreasing from 1.89 to 1.71, which clearly indicates the deposition of the Ag on the ZnO substrate. Same results were highlighted more clearly in the Figure 12.
The concentration of the Ag NPs solution has been calculated in every step of the electrophoresis process using the Beer-Lambert law. As shown in Figure 12(A) by decreasing the concentration of the Ag in the solution the corresponding absorption values of the solution were also decreasing. Initial concentration of the Ag NP solution used during the electrophoresis was $6.74 \times 10^{-4}$ M in 89 ml of ethanol.

$$A = \varepsilon b C$$  \hspace{1cm} (1)

Where $\varepsilon$ is the molar absorptivity coefficient, $b$ is the path length of the sample or the width of cuvette (cm) and $C$ is the molar concentration of the compound.

On the basis of the obtained graphs and the Beer-Lambert relation, the number of loaded Ag NPs on the ZnO nanorods can be simply determined. (Table 1)

<table>
<thead>
<tr>
<th>sample</th>
<th>Abs</th>
<th>concentration (M)</th>
<th>mol of deposited Ag</th>
<th>number of deposited Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.891</td>
<td>$6.74 \times 10^{-4}$</td>
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<td>0</td>
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<tr>
<td>2</td>
<td>1.8453</td>
<td>$6.577 \times 10^{-4}$</td>
<td>1.894$\times 10^{-4}$</td>
<td>1.140$\times 10^{20}$</td>
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<tr>
<td>3</td>
<td>1.8323</td>
<td>$6.530 \times 10^{-4}$</td>
<td>2.432$\times 10^{-4}$</td>
<td>1.464$\times 10^{20}$</td>
</tr>
<tr>
<td>4</td>
<td>1.8236</td>
<td>$6.499 \times 10^{-4}$</td>
<td>2.793$\times 10^{-4}$</td>
<td>1.681$\times 10^{20}$</td>
</tr>
<tr>
<td>5</td>
<td>1.79</td>
<td>$6.380 \times 10^{-4}$</td>
<td>4.185$\times 10^{-4}$</td>
<td>2.519$\times 10^{20}$</td>
</tr>
<tr>
<td>6</td>
<td>1.71</td>
<td>$6.094 \times 10^{-4}$</td>
<td>7.501$\times 10^{-4}$</td>
<td>4.515$\times 10^{20}$</td>
</tr>
</tbody>
</table>

### 4.1.2 Analyzing the electrophoretic deposition of Au NPs on ZnO nanowires

Au nanoparticles have been deposited on the ZnO nanowires with the same experimental setup as mentioned before for depositing silver NP. The initial concentration of the Au NPs was $5 \times$
10^{-3} \text{ M} \text{ in 60 ml of distilled water and the difference between the potential of electrodes was 10 V. Considering the initial concentration of the solution and by using the Beer-Lambert law, as it was mentioned in equation 1, molar absorptivity coefficient of the solution was measured to be } \varepsilon = 812.68 \text{ } \text{L mol}^{-1} \text{ cm}^{-1}. \text{ As it is shown in Figure 13, by electrophoresing the Au NP on the ZnO NRs substrate the absorption spectra of the solution were correspondingly decreasing.}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{absorption_spectra.png}
\caption{Absorption spectra of the samples during the electrophoresis process.}
\end{figure}

The concentration of Au NP during the electrophoresis process in each step of the depositing process has been calculated by taking samples from the electrophoresis solution and measuring the absorption data. Using the linear fitting of the beer-lambert law the corresponding graph of the concentration versus time is plotted in the Figure 14 (A). As it is also shown in Figure 14 (B) the absorbance of the solution is clearly decreasing by moving toward the electrophoresis process.
Obtained values for concentration of deposited Au NPs on the substrates were also presented below.

Table 2: Calculated amount of deposited Au NP on the ZnO substrate using Beer-Lambert law.

<table>
<thead>
<tr>
<th>sample</th>
<th>ABS</th>
<th>concentration (M)</th>
<th>mol of deposited Au</th>
<th>number of deposited Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.0634</td>
<td>5x10^{-3}</td>
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<td>0</td>
</tr>
<tr>
<td>2</td>
<td>4.01001</td>
<td>4.934x10^{-3}</td>
<td>1.094x10^{-3}</td>
<td>6.59x10^{20}</td>
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<tr>
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<td>4.766x10^{-3}</td>
<td>3.884x10^{-3}</td>
<td>2.34x10^{21}</td>
</tr>
<tr>
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<td>4.289x10^{-3}</td>
<td>1.184x10^{-3}</td>
<td>7.13x10^{21}</td>
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<tr>
<td>5</td>
<td>3.4327</td>
<td>4.223x10^{-3}</td>
<td>1.293x10^{-3}</td>
<td>7.79x10^{21}</td>
</tr>
</tbody>
</table>

4.2 Scanning Electron Microscopy (SEM) and Energy Dispersion Spectrometry (EDS)

The morphology and composition of the prepared ZnO nanowires are characterized using a Joel JSM-IT300 scanning electron microscope in an accelerating voltage of 20 kV (secondary electron mode). Figure 15 shows the SEM images of the produced ZnO NWs fabricated by the hydrothermal method and then impregnated with different NPs. In all images the uniform distribution and alignment of the ZnO can be clearly observed. SEM analysis revealed that the ZnO NWs grow nearly vertically and have a Wurtzite structure with hexagonal cross section. Even after deposition of the NPs, no obvious changes were observed in the morphology of the ZnO NWs. The areal density of the NWs is estimated to be around 23/μm².
Figure 15: SEM and EDS data of ZnO samples impregnated with (A) Ag NPs, (B) Au NPs and (C) Cu NPs.

EDS analysis reveal the presence on NPs with various concentrations in the structure of ZnO films. However, concentration of the NPs cannot be accurately estimated with EDS spectra. In the next section, results of the same analysis applied on TiO$_2$ NWs is presented.

Figure 16: SEM and EDS data of TiO$_2$ samples impregnated with (A) Ag NPs, (B) Au NPs and (C) Cu NPs.

The morphological structure of the TiO$_2$ NWs is shown in the Figure 16. After deposition of the different NPs the NWs kept their original shape (as far as we could observe). Corresponding EDS signal after deposition of the NPs is also presented in Figure 15.
4.3 X-Ray diffraction (XRD) analysis

XRD was used to investigate the crystalline structure of our undecorated ZnO nanorods and also the decorated ZnO with Ag and Au NPs during the 40 min of the X-ray radiation cycle. However, for all our decorated samples with NPs no remarkable change in the obtained spectra can be observed. The obtained XRD graph is shown in Figure 17. The very intense peak at 2Ө=34.5 is assigned to (002) plane of ZnO NWs which is the desired preferential orientation of the ZnO nanoarrays. In addition, XRD analysis, confirm the observed structure of ZnO NWs via SEM.

![XRD graph](image)

*Figure 17: XRD evaluation of ZnO samples after deposition of Ag NPs and Au NPs.*

4.4 Reflectance spectroscopy

Optical characterization of the as-prepared samples and precursors was carried out by a Cary 5000 UV-vis spectrophotometer in various optical ranges of incident lights.

Figure 18 shows the reflectance spectra of ZnO samples before and after deposition of NPs as well as absorption spectra of Ag, Au and Cu nanoparticles in the colloidal suspension. The blue curves represent the absorption spectra of the NPs diluted in their suspension. consequently, pertaining plasmonic peak for silver, gold and copper NPs can be observed in 400 nm, 520 nm and 590 nm, respectively.
Figure 18: Reflectance spectra of ZnO NWs before and after deposition of: A= Ag NPs, B= Au NPs and C= Cu NPs. Blue curve represents the absorbance of NPs in colloidal suspension.

After deposition of plasmonic NPs on the bare ZnO samples, a plasmonic drop in the reflectance spectra of the impregnated samples corresponding to excitation wavelength of the used NPs is observed.

For instance, in Figure 18 (A) the plasmonic peak of the Ag NPs capped with PVP molecules, is located at 400 nm, which is as well visible in the optical spectra pertaining to ZnO NWs uploaded with the plasmonic particles, although shifted towards higher wavelength (410 nm).
Figure 19: Reflectance spectra of TiO$_2$ NWs before and after deposition of; A= Ag NPs, B= Au NPs and C= Cu NPs. Blue curve represents the absorbance of NPs in colloidal suspension.

Same strategies have been employed for TiO$_2$ NWs substrates prior and after deposition of the NPs as shown in Figure 19. A similar drop can be detected in the reflectance spectra of the samples after deposition of different NPs due to mentioned plasmonic properties of uploaded NPs. Having said that, the small displacement in the position of the plasmonic peak between absorption spectra and reflectance of the impregnated samples in Figure 19 (A) is reported, probably due to dielectric change of Ag NPs environment in suspension and on the substrates.

Absorption spectra of the Cu NPs in Figure 18 (C) and Figure 19 (C) present a relatively weaker plasmonic peak compared to Ag and Au NPs, because their free-electron behavior is due to their notable dielectric functions. Cu NPs plasmonic responses to UV-vis at around 600 nm is believed to be generated by interband transitions between the valance and Fermi energy level of the copper [54]. This can be in principle responsible for the comparatively weaker resonance shift of the Cu NPs.
4.5 Photoluminescence (PL) spectroscopy

Photoluminescence (PL) spectroscopy was performed using a Cary Eclipse fluorescence spectrophotometer under 325nm excitation wavelength. The obtained PL spectra of bare ZnO and Ag NPs impregnated samples is shown in Figure 20. The PL spectra of bare ZnO NWs consists of a strong emission at 388 nm and a relatively weak and broad emission at around 550nm in the green light region. The sharp peak at 388 nm is assigned to the direct band-edge emission of the ZnO nanorods, and the weak broad peak can be attributed to the structural and morphological defects of ZnO nanorods, which create charge relaxation and excessive electron-hole recombination.

The blue curve in Figure 20 shows the PL spectrum of a ZnO sample deposited with uncapped Ag NPs. In this case Ag NPs were directly seeded on the ZnO NWs substrate. The PL result displays a slight enhancement of band edge emission of the ZnO NWs, while the emission of the ZnO defects in the green region do not have a significant change.

Figure 20: PL spectroscopy of bare ZnO sample (black) and ZnO/Ag NPs (blue).

In order to study the LSPR mechanism of NPs on the ZnO substrates, a 10 nm Al₂O₃ layer functioning as an insulator spacer layer was deposited between Ag NPs and ZnO NWs. The spacer layer was deposited using an ULTRATECH atomic layer deposition system.

Even after deposition of an insulating Al₂O₃ spacer layer between NPs and ZnO substrate, the plasmonic effect of NPs were considerable. The PL spectra in Figure 21 show that the deposition of Ag NPs on ZnO-Al₂O₃ slightly increases the near band edge emission of ZnO. A possible explanation for this increase in PL intensity for samples after Ag uptake with the Al₂O₃ spacer is contained in refs. [63,64]. Specifically, it would be possible that PL emission from defects (broad band in the 500-600 nm range) is transferred through Fermi energy level of Ag NPs to the bandgap emission from ZnO.
In order to illustrate the SPR effect of Ag NPs on ZnO substrates, we use the predicted plasmonic mechanism of Au NPs on ZnO NWs. The band alignment sketch of conduction band, valence band and defect emission of ZnO NWs along with Fermi energy level of plasmonic NPs are plotted in Figure 22. Normal hydrogen electrode (NHE) is used as reference line. It can be seen that, electrons in the defect meta stable state of ZnO can excite the Fermi energy level of Au NPs and later on move toward the higher energy states and eventually conduction band of ZnO NWs. Thus, electrons neglect the defect state of NWs and enhance the band gap emission of ZnO NWs [66].
5 Conclusion

In this thesis, experimental work for investigating the plasmonic effect of NPs on wide band gap semiconductors was performed using state of the art devices suitable for this studies. The measurements were carried out at Lulea University of Technology material’s division and experimental physics department.

In this project, we introduced a low temperature hydrothermal method for the synthesis of ZnO and TiO$_2$ semiconductor NWs films over FTO glass substrates. The advantage of this particular method is that it can be cost effective and without complicated compounds, while all chemical reactions involved are facile and well-controlled.

Different synthetic approaches have been employed to synthesize various metal NPs including Ag NPs, Au NPs and Cu NPs.

Here, we illustrated the Electrophoresis method as the main route for deposition of Metal NPs on the wide band gap MOs semiconductors. The electrophoretic deposition used as a simple direct uptaking technique for loading metal NPs on MOs substrates.

Presented PL results demonstrated that integrated ZnO NWs with Ag NPs can increase the near band edge (UV) emission of ZnO NWs at 388 nm and therefore boost up their potential application in optoelectronic and photocatalytic applications. Our results suggested that, versatile approaches of NPs deposition combined with inserting and Al$_2$O$_3$ spacer layer can clearly explain the significant UV emission behavior of ZnO semiconductors through coupling with plasmonic effect of metal NPs.

The plasmonic peak of the metal NPs in the UV-vis absorption spectra of diluted particles was recorded. Electrical properties of ZnO and TiO$_2$ NWs prior and after loading of the plasmonic particles has been investigated. Reflectance spectra of the produced specimen presented the enhancement of light absorption in the relative absorption region of plasmonic NPs.

The obtained results in this report provided a crucial concept for the future design of optoelectronic devices such as photovoltaic devices and biosensors.
Future work and Outlook

- The mechanism of interactions between plasmonic NPs and the substrate can be further analyzed by photoinduced absorption (PIA) spectroscopy. PIA also known as pump probe method is a technique in which a pulsed beam of light, generated from a laser or LED, excites an off interest specimen whilst, the excited sample is being analyzed using a probe. PIA method is mostly used in fundamental processes like dynamics of excited material such as dyes in dye sensitized solar cells (DSSC) to investigate the basic mechanisms like charge separation and recombination.

- Synthesis of different plasmonic NPs with various shapes and structures (hybrid or core-shell structures) can provide good set points for increasing the plasmon enhanced absorption of semiconductors.

- The studies can be further developed by creating a full MOs heterojunction SCs and investigating their conversion efficiency and light absorption efficiency.

- Effect of NPs concentration on the plasmonic resonance

![Figure 23: Reflectance of ZnO samples before (black lines) and after (blue lines) Ag NP deposition by (a) 210 s, (b) 8 min and (c) 20 min of electrophoresis. Absorbance (orange series in (a-c)) of Ag NPs in the colloidal suspension.](image)

One of the important factors affecting the plasmonic enhancement of impregnated samples is the concentration of metal NPs (Figure 23). By increasing the deposition time of the Ag NPs from 210 s to 8 min the plasmonic peak of Ag NPs becomes more distinctive, whilst after increasing the deposition time to 20 min the plasmonic peak is relatively weaker compare to the sample with 8 min of deposition. Consequently, finding a relation between number ofuptaken NPs to the obtained plasmonic peak can be the matter of interest.
7 Acknowledgement

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8 References


