CHAPTER 1

INTRODUCTION

1.1 Introduction

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular, and macromolecular scales, where properties differ significantly from those at a larger scale. Therefore, nanotechnologies are the intensive branch of science that interesting in design, characterization, production, and application of structures, devices, and systems by controlling shape and size on the nanoscale. So, nanomaterials cross the boundary between nanoscience and nanotechnology and link the two areas together, so these definitions are very appropriate. It is recognized that the size range that provides the greatest potential and, hence, the greatest interest is level between approximately 1 to 100 nm at least one dimension with different shapes of spherical nanoparticles, nanorods, nanoribbons, nanobelts and nanoplates. In addition, these nanomaterials exhibit very interesting size dependent electrical, optical, magnetic, and chemical properties that cannot be achieved by their bulk counterparts. For many future applications, the synthesis of uniform-sized of nanomaterials is of key importance, because the electrical, optical, and magnetic properties of these nanocrystals are strongly dependent on their dimensions [1-5].

Any solid or liquid system possesses at most two-dimensional order of periodicity called “thin film”. Properties of thin film often differ significantly from those of bulk due to surface and interface effects, which may dominate the overall behavior of these films. Thin films are of particular interest for fabrication of large area arrays, solar selective coatings, solar cells, photoconductors, sensors, antireflection coatings, interference items, polarizers, narrow band filters, IR detectors, wave guide coatings, temperature control of satellites, photothermal solar coatings etc. [6].

1.2 Transition Metal Oxides (TMOs)

Transition metal oxides (TMOs), such as zinc, copper, tungsten, titanium oxides and etc., constitute an important class of inorganic solids exhibiting a very wide variety of structures, electronic, optic and magnetic properties. Nanostructured TMOs is a particular class of nanomaterials, are the indisputable prerequisite for the development of various novel functional and smart materials. TMOs have been received increasing attentions as a class of materials because they have unique physical and chemical properties and wide applications in catalysis, energy storage, sensors, lithium ion batteries, antibacterial and biological medicine. The physical and chemical properties are strongly dependent on the sizes, shapes, compositions, and structures of the nanocrystals. Interesting phenomena such as remarkable increase in surface-to-volume ratio, significant change in surface energy, and quantum confinement effects occur when TMOs are reduced to nanoscale dimension. These phenomena result in a variety of new physical and chemical properties that are not feasible for materials with bulk dimensionality. Therefore, the manipulation of well-controlled synthesis and fabrication of nanostructured TMOs with different sizes, shapes, chemical compositions, and structures is crucial in the advancement in nanoscience and nanotechnology. Several different synthetic strategies have been explored for the synthesis of TMOs nanomaterials, such as the hydro-solvothermal synthesis, pulsed laser deposition, chemical vapor deposition (CVD) and the traditional sol–gel method. However, the high processing temperatures, expensive equipment, hazardous chemicals and rigorous manipulation limited the large production of TMOs and their applications. Therefore, it is significant to develop a general synthetic method for TMOs nanostructures in aqueous medium, which could make the synthesis of nanomaterials more rational and environment-friendly [7-9]. They are many kinds of TMOs that have been interested, but in the thesis focused on some of TMOs, ZnO and CuO.

1.2.1 Zinc Oxide (ZnO)

ZnO is the most widely investigated TMOs a II–VI compound n-type semiconductor with unique properties such as transparency in the visible and high infrared reflectivity, acoustic characteristics, high electrochemical stability and excellently electronic properties. The band gap energy of ZnO is 3.37 eV and a large excitonic binding energy of 60 meV at room temperature. The direct wide band-gap of ZnO makes the semiconductor a good candidate for optoelectronic applications and the large exciton energy helps to employ the excitonic recombination process as a lasing mechanism [7, 10-13].

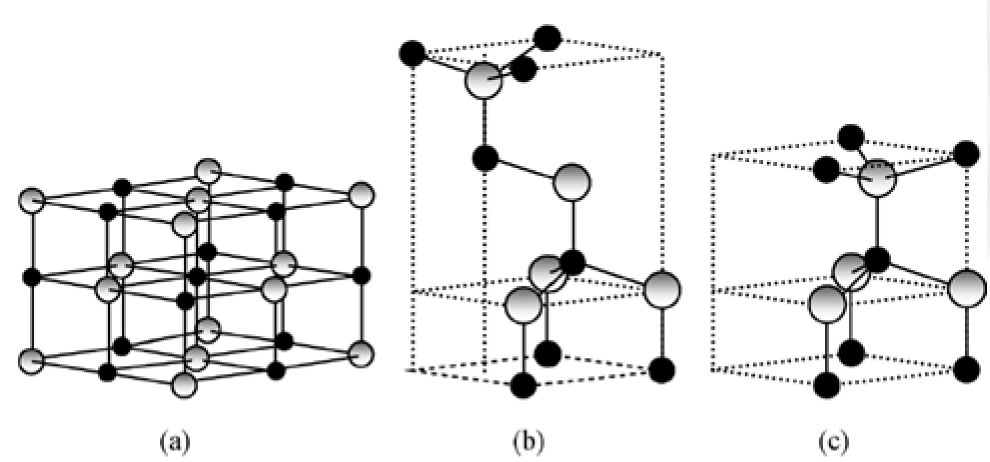

Figure 1.1 Stick and ball representation of ZnO crystal structures: (a) cubic rock salt, (b) cubic zinc blende and (c) hexagonal wurtzite. Shaded gray and black spheres denote Zn and O atoms, respectively [12,13].

Figure1.1 shows either a hexagonal wurtzite, cubic zinc-blende (which are both tetrahedral) or rarely rocksalt structure (which is formed at very high pressures). In wurtzite structure, every Zn atom is surrounded by four oxygen atoms. In zinc-blende structure, each oxygen atom is surrounded by four Zn atoms in a similar fashion. At ambient temperatures and pressure wurtzite is the stable polymorph and a stable zinc-blende structure is generally obtained when ZnO is grown on cubic substrates.

ZnO exists in wurtzite and zinc-blende crystal structures, however, at ambient temperature and pressure, ZnO crystallizes normally in a wurtzite structure with a hexagonal lattice that has two interconnecting sub-lattices of Zn^{2+} and O^{2-} with the zinc ion surrounded by tetrahedral oxygen ions and vice versa. This tetrahedral coordination gives rise to a polar symmetry along the hexagonal axis, which is responsible for a number of the physical and chemical properties of ZnO, including piezoelectricity and spontaneous polarization. The structure of ZnO is a key factor in crystal growth, etching and defect generation. The large piezoelectric coefficient of ZnO has allowed for the development of surface acoustic wave (SAW) devices that can operate at higher frequencies than other devices. The variation in electrical properties such as conductivity is dictated by the presence of oxygen vacancies, shallow zinc interstitial, hydrogen impurity and other donor type point defects. Moreover, the ZnO near-surface region can be highly conductive due to H donors in this region and a large density of near-surface electrons.

ZnO is a material of technological importance due to its unique combination of piezoelectric, conductive, and optical properties. It is a polar semiconductor material with two crystallographic layers that have opposite polarity and different surface relaxation energies, which lead to a higher growth rate along the c-axis, e.g., the formation of nanorod-like vertical structures. There are made up of alternative layers of Zn^{2+} and O^{2-} ions stacked in the [001] direction, forming the Zn-O bilayers (Fig. 1.2). Each bilayer is stacked on top of another bilayer in the [001] direction, in the stacking sequence AaBbAaBb, forming a hexagonal close packed structure. Within each bilayer, there exists a spontaneous polarization due to the net electric dipole moment pointing from O^{2-} to Zn^{2+} [7, 14-16].

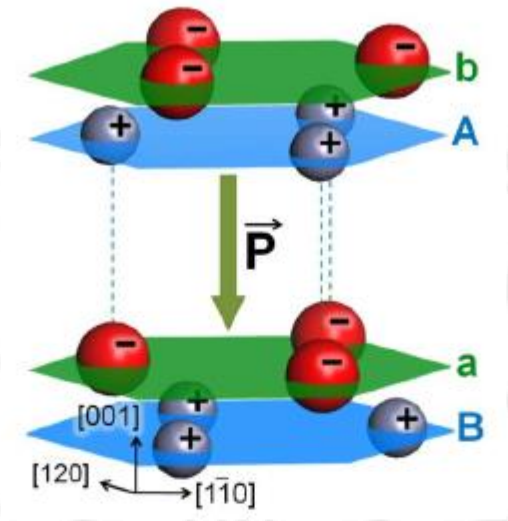

Figure 1.2 ZnO has a noncentrosymmetric crystal structure that is made up of alternate layers of positive and negative ions, leading to spontaneous polarization. The pseudoferroelectric switching involves the reversal of these dipole moments [14].

Table 1.1 Physical properties of ZnO at room temperature (300 K).

Properties	Value
Density	5.606 g/cm^3
Melting point	2248 K
Dielectric constant	8.66
Exciton binding energy	60 meV
Band gap (Eg)	3.4 eV direct
Hole mobility	5-50 m^2/Vs

1.2.2 Copper Oxide (CuO)

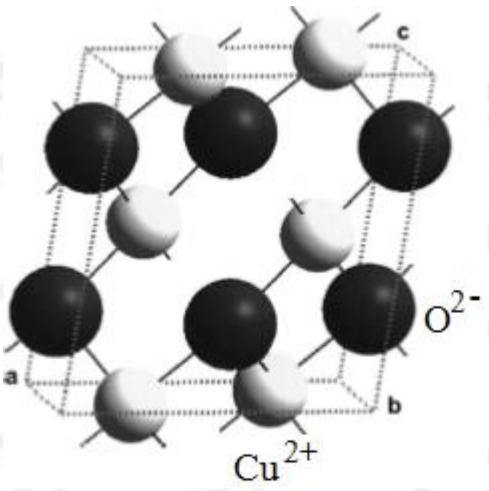

Figure 1.3 CuO monoclinic crystal structure [17]

Copper oxide or Cupric oxide (CuO) has been a hot topic among the studies on TMOs because of its interesting properties as a p-type semiconductor with a narrow band gap (1.2 eV in bulk) and as the basis of several high-temperature superconductors and giant magneto resistance materials. CuO nanostructures with large surface areas and potential size effects possess superior physical and chemical properties that remarkably differ from those of their micro or bulk counterparts. These nanostructures have been extensively investigated because of their promising applications in various fields such as gas sensors, bio-sensors, nanofluid, photodetectors, energetic materials (EMs), field emissions, supercapacitors, removal of inorganic pollutants, photocatalysis, and magnetic storage media [7,17-19].

The crystal structure of CuO was first determined by Tunnel in 1933 and was then refined by single-crystal X-ray methods in 1970. Contrary to the usual rock-salt structure of other 3d transition-metal monoxides, the CuO crystal structure is monoclinic with C2/c symmetry and four formula units per unit cell. The Cu^{2+} ions are at centers of inversion symmetry in a single fourfold site 4c (1/4, 1/4,0), and the oxygen ions occupy site 4e (0,y,1/4) (Fig. 3). The special atomic positions for Cu are (1/4, 1/4, 0), (3/4, 3/4, 0), (1/4, 3/4, 1/2), and (3/4, 1/4,1/2) and for oxygen are (0,y, 1/4), (0,1/2 + y, 1/4), (0, y, 3/4), and (1/2,1/2-y,3/4) with y = 0.416 [17].

Table 1.2 Physical properties of CuO at room temperature (300 K). [17]

Properties	Value
Density	6.31 g/cm^3
Melting point	1200 °C
Stable phase at 300 K	Monoclinic
Dielectric constant	18.1
Refractive index	1.4
Band gap (Eg)	1.21-1.55 eV direct
Hole mobility	0.1-10 m^2/Vs

1.3 Synthesis Method of TMOs

Consequently, various nanostructured TMOs have been synthesized by diverse chemical, physicochemical, and physical strategies**.** To comparing with their micro or bulk counterparts, nanostructured TMOs exhibit unique structural characteristics and size confinement effects as well as novel properties. These properties contribute to the potential of TMOs as candidates for both theoretical studies and practical applications in micro/nanodevices. The design of nanostructures TMOs has been the basis of many advances in technology for the last decade.

In general, manufactured nanostructures TMOs can be classified according to their chemical composition and properties. They can be produced by a huge range of procedures which can be grouped into top-down and bottom-up strategies [3,20].

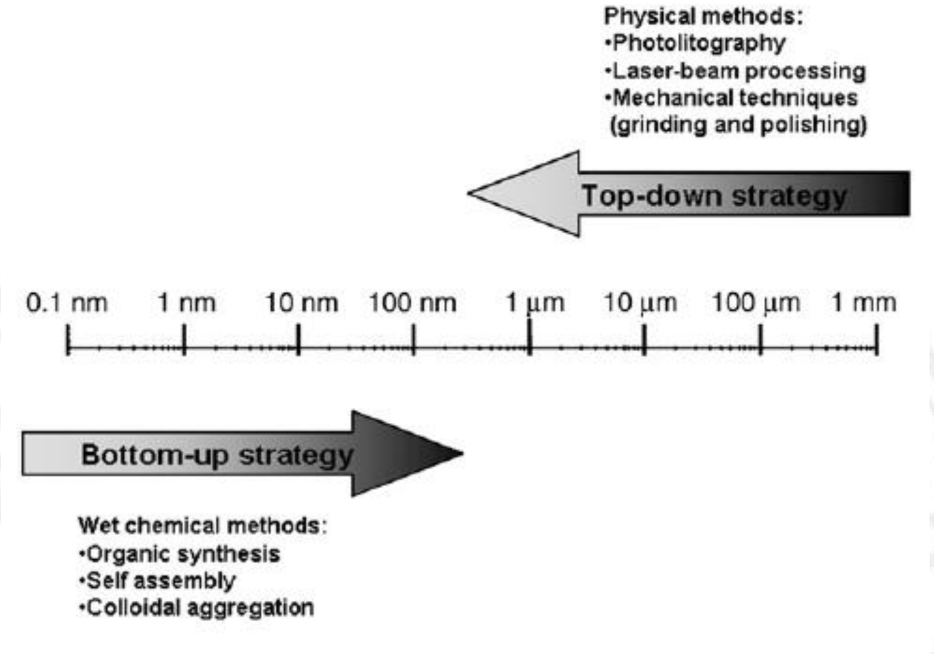

Figure 1.4 Top-down and bottom up strategies [3].

Top-down of nanomaterials approaches are defined as those by which or well-organised assemblies are directly generated from bulk materials or involves breaking down larger particles of matter to particles of only nanometers in dimension. The majority of the top-down strategies involve physical or chemical methods such as mechanical milling. Dry milling of wheat bran has potential as a bioactive food ingredient, but is not widely used at present. Homogenization is also a top down size reduction mechanism. It is a well-established industrial process which uses pressure to reduce the size of fat globules. It is used globally in the dairy industry. The use of lasers and vaporization followed by cooling are other top down methods of nanomaterials [10,13,17,20,21].

Bottom-up strategies involve molecular components as starting materials linked with chemical reactions, nucleation and growth process to promote the formation of more complex clusters. Nanostructures TMOs differ from larger materials in that the number of atoms at the surface and their physical properties are different from those of bulk materials. Properties associated with the bulk materials are averaged properties, such as density, resistivity and magnetization and the dielectric constant. Critically, however, many properties of these materials change over at the nanostructures TMOs. These differences arise from the small size and large number of surface atoms of the particles and related effects**.** Methods of bottom up manufacture include crystallization, layer-by-layer deposition, solvent extraction/ evaporation, self-assembly, microbial synthesis and biomass reactions. This approach is capable of producing more complex molecular structures by design based on self-organization of biological compounds. It involves arranging molecules step by step to design the particles so that they have specific features. The physical and chemical properties of nanomaterials vary as a function of size, shape and surface chemistry. Thus, new synthetic strategies are vital for the development of novel nanomaterials [10,13,17,20,21].

Several different synthetic strategies have been explored for the synthesis of TMOs nanomaterials, such as the solvothermal synthesis, pulsed laser deposition, chemical vapor deposition (CVD) and the traditional sol–gel method. Various organic reactions of metal oxide nanoparticles synthesis in nonaqueous medium were also reported. However, the high processing temperatures, expensive equipment's, hazardous chemicals and rigorous manipulation limited the large production of transition metal oxides and their subsequent applications. Therefore, it is significant to develop a general synthetic method for transition metal oxides nanostructures in aqueous medium, which could make the synthesis of nanomaterials more rational and environment-friendly.

There are two primary approaches for the fabrication of TMOs nanomaterials: physical techniques based (gas phase synthesis) and chemical techniques based (solution phase synthesis) [10,13,17,20,21].

1.3.1 Physical techniques based

Physical techniques based are the dry methods to obtain TMOs nanostructures. In these methods, one can obtain TMOs nanostructures with adequate control; however, these techniques typically require harsh temperature conditions (500-1,500°C) and low pressure. Most commonly employed physical techniques to grow TMOs nanostructures involve the carbothermal reduction process, thermal evaporation, and chemical vapor deposition (CVD) in addition to thermal evaporation, typically require high temperatures and pressures as well as particular substrates and result in low product yield. These methods produce high quality TMOs nanostructures; however, the methods are the high processing temperatures, expensive equipment's, hazardous chemicals and rigorous manipulation limited the large production of TMOs and their subsequent applications [10,13,17].

1.3.2 Chemical techniques based

Chemical techniques based are very common and effective ways to prepare various TMOs nanostructures with good control of shape, composition and reproducibility. The growth process is carried out in a liquid, such as an aqueous or organic solution, at a relatively low temperature (< 200°C). Currently, the solution phase synthesis technique has emerged as one of the most important methods due to its numerous advantages, such as low production cost, scalability and reduced temperature. These methods include hydrothermal, solvothermal processes, solution–liquid–solid (SLS) and capping agents/surfactant assisted synthesis. Further, the growth direction can be controlled by adjusting the growth process parameters, such as the reagent of interest, stoichiometry, temperature and pH in the methods. Moreover, the synthesis parameters can be rationally tailored throughout the entire process, which is beneficial for more precise control of compositions, sizes, and dimensions of the resulting materials. For example, amine compounds are often used to direct growth in the c-direction, whereas citrate inhibits c-direction growth and directs the crystal shape into thicker rods or even plates. Thus, chemical techniques provide convenient, facile manipulation, potential for scale-up and a lower temperature pathway for the fabrication of the desired TMOs nanostructures. Recently, electrochemical techniques have also emerged as a new synthesis method for TMOs nanostructures. So, a great number of chemical techniques have been documented in the last few years. Among a variety of solution-based synthetic methods, hydrothermal and chemical precipitation techniques have been widely used to synthesize TMOs nanostructures [10,13,17,21].

a) Hydrothermal Synthetic Method

Figure 1.5 Autoclave for used in Hydrothermal/Solvothermal method.

Hydrothermal synthetic method, which the reactions are conducted in water as reaction medium in a pressurized sealed reaction container and reaction temperature over the critical point of a solution, raised above 100°C, has been widely used to generate different nanomaterials because its reaction system is simple/green, with convenient post treatment [21]. Autogenous pressure which is self-developed and not externally applied is generated under these conditions. The pressure within the sealed reaction container increases dramatically with temperature, but also will depend on other experimental factors, such as the percentage fill of the vessel and any dissolved salts. A high percentage fill allows access to pressures of hundreds of atmospheres when the temperature is below the critical point of water, and even below 200ºC. Furthermore, the hydrothermal method exhibits the following advantages [13]:

1) Numerous inorganic salts can be well dissolved in water, allowing a very flexible adjustment of the source of the metal ions depending on the requirements.
2) Water is low-cost, non-toxic, and environmentally friendly.
3) Small coordinating molecules can be easily applied to modulate the growth of the final nanocrystals.
4) The strong polarity of water may be favorable to the oriented growth of nanocrystals.

b) Chemical Precipitation Methods

Chemical precipitation synthesis is similar to the hydrothermal method with a reaction also occurring in the solution, but the chemical reactions can be conducted in an open container with a relatively low reaction temperature (normally below 100°C). This process can be simply defined as the chemical reaction between the precursors to produce monomers that subsequently aggregate into final resulting materials [17].

1.4 Applications of TMOs

This section has been focued on the application of ZnO and CuO. These fields include LIBs, sensors, solar cells, photodetectors, photocatalysis, antibacterial and etc.

1.4.1 Lithium-ion batteries (LIBs) [8,17]

To date, nanostructure TMOs (where the metal may be Fe, Co, Ni, or Cu) have been considered as promising anodes for LIBs because of their high theoretic capacity and excellent cycling capacity retention property. Among these TMOs, CuO is extensively investigated because of high theoretic capacity (670 mA h/g), low cost, environmental benignity, easy production, and easy storage, among others. The large volume variation during the lithium uptake/release process is one of the most important issues restricting its application in LIBs, which results in severe mechanical strains and very rapid capacity decay. In this regard, considerable efforts have been made to use nanoarchitectured electrodes to overcome this drawback and improve the electrochemical performance. Various CuO nanostructures, including 0D nanoparticles, 1D nanowire and nanorods, and other complex 2D/3D hollow nanostructures, have been developed using different synthetic strategies to optimize the electrochemical performance of CuO. Well defined unique hierarchical or hollow nanostructured CuO has been verified as a good candidate for LIBs because of its high surface area, low material density, and surface permeability.

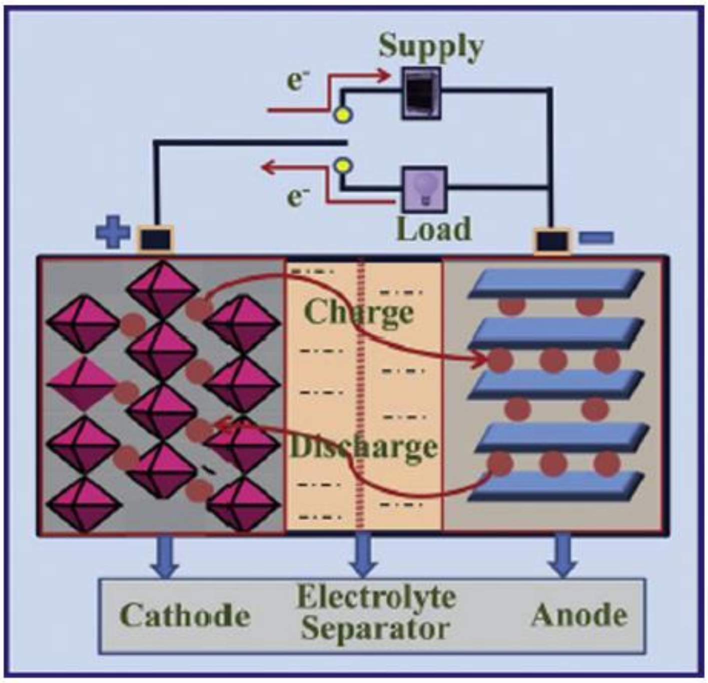

Figure 1.6 Schematic illustration of a typical LIB and the electrochemical processes [17].

1.4.2 Sensors [10,17]

Semiconducting TMO gas sensors are advanced sensor types. Since the pioneering reports on their gas sensitivity at elevated temperatures in the 1950s, gas sensors based on these TMOs for detection of hazardous, flammable, and toxic gases has been increasingly developed because of their small dimension, low cost, and high compatibility with microelectronic processing. The physical and chemical properties of nanoscale materials are strongly influenced by their dimensional constraints and morphologies. Gas sensors based on nanostructured TMOs are expected to exhibit better performance than their bulk or microcounterparts. In this regard, MO nanostructures, such as 1D nanowire, 1D nanorods, 2D nanosheets, 3D nanoflowers, and complex hierarchical architectures, have attracted considerable interest for their potential as building blocks for fabricating gas sensors because of their high effective surface areas. Among various TMOs, CuO has the unique property of being intrinsically p-type and is advantageous because of its low cost, high stability, nontoxicity, and capability for electron transfer. Therefore, CuO nanostructures have been extensively investigated as good candidates for sensing applications. Gas sensors based on CuO nanostructures were operated by measuring the resistance changes when they are exposed to reducing or oxidizing gases. A suitable operation temperature is crucial to the gas sensing capability of CuO because it enhances the sensitivity and reduces the response and recovery time. Coating of noble metal catalysts, such as Ag, Au, Pd, and Pt, on the surface of CuO nanostructures will enhance their sensing properties because they can act as adsorption sites for analysts or as surface catalyst [17].

The sensing mechanism of gas sensors based on p-type CuO is contrary to n-type TMOs. In the air, oxygen molecules are adsorbed onto the CuO surface forming oxygen ions (O^-, O_2^- O^{2-}) charging it negatively. If a reducing species, such as NH_3 is present, it oxidizes and releases a negative charge (electron). In this regard, the electron transfer from oxygen ions (O^-, O_2^- O^{2-}) to CuO results in decreased hole density and thus decreased conductance. Meanwhile, the number of oxygen ions (O^-, O_2^- O^{2-}) adsorbed on the surface of CuO is also reduced, which leads to the decrease in the magnitude of the negative quasi-gate resulting in further decrease inconductivity. Exposure to oxidizing gas, such as NO_2, likely results in the occurrence of charge transfer from the CuO to the NO_2 as governed. The electron transfer from the CuO to the NO_2 results in the lowering of the quasi-Fermi level and thus increases free hole density and enhances conductance. Additionally, the negatively charged chemisorbed NO_2 molecule at the CuO surface may act as a negative gate bias and increase CuO conductance. The proposed sensing mechanisms of NH_3 and NO_2 are shown in Fig. 1.7.

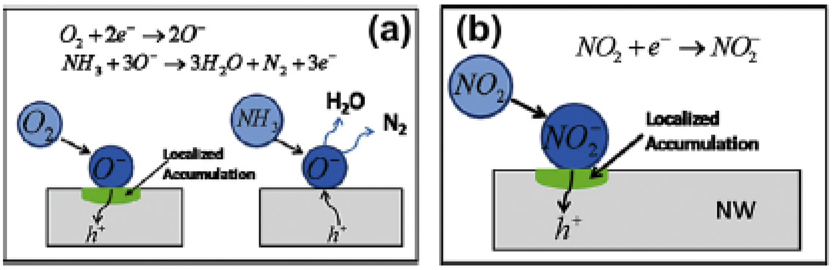

Figure 1.7 Schematic of the proposed sensing mechanism of NH_3 and NO_2 [17].

A number of studies have focused on the development of novel TMOs nanostructures for the detection of a wide range of gases, such as organic gases, hydrogen sulfide (H_2S), CO, NO_2, ethanol gas, NH_3, HCN, and humidity.

1.4.3 **Solar cells** [17,22]

CuO, as a p-type semiconductor with the band gap energy in the 1.2–2.1 eV range, has been broadly examined for photovoltaic applications because of its low cost, high solar absorbance, low thermal emittance, non-toxicity, and simple manufacturing process. Moreover, CuO is very promising for use in solar photovoltaic because of its excellent stability, good electrical properties, and high carrier concentration of CuO.

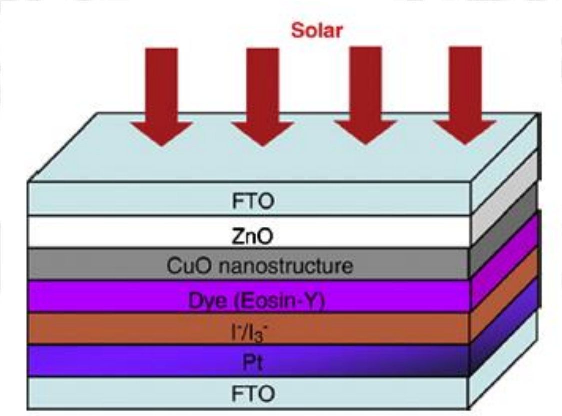

Figure 1.8 Schematic diagram of DSSC structures withdifferent photoelectrods for ZnO/CuO layer [17].

1.4.4 **Photodetectors** [17]

Photodetectors or photoconductivity is a well-known property of semiconductors in which the electrical conductivity changes (usually increases) because of incident radiation. These changes involve several successive or simultaneous mechanisms including absorption of the incident light, carrier photogeneration, and carrier transport (including carrier trapping, detrapping, and recombination). A mechanism using a ZnO nanowire as the model system has been comprehensively outlined (Fig. 1.9). With large surface-to-volume ratios and Debye length comparable to their small sizes, TMOs nanomaterials have already displayed superior sensitivity to light in experimental devices. Thus, the fabrication and characterization of novel nanostructures for applications in photodetectors based on different TMOs nanomaterials has been extensively explored. CuO is intrinsically a p-type semiconductor with a low band gap (1.2–2.0 eV), indicating its potential in photodetection and optical switching applications in the visible range in which other MOs with their larger band gaps fail to perform.

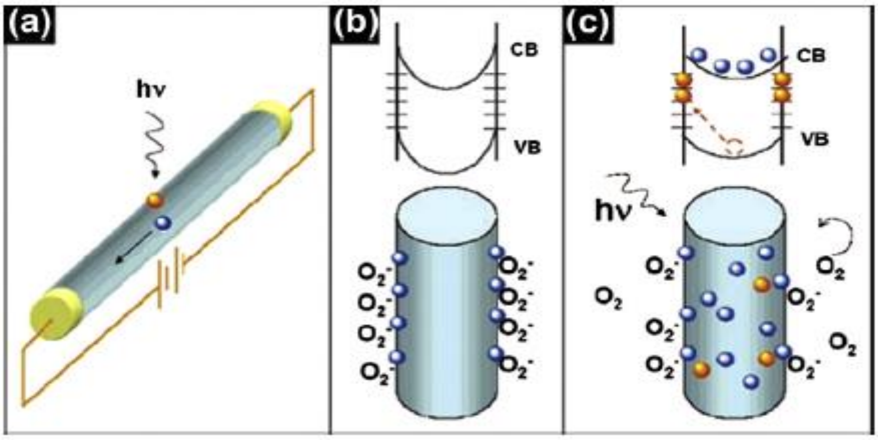

Figure 1.9 Photoconduction in a nanowire photodetector: (a) schematic of a nanowire photodetector. Trapping (b) photoconduction and (c) mechanism in ZnO nanowires [17].

1.4.5 **Photocatalysis** [17,20]

Organic dyes, which are widely used in various industrial processes, form an integral part of industrial wastewater. Dye removal and degradation has been a subject of concern worldwide because of the potential toxicity and visibility of dye in surface water. Numerous processes and methodologies have been developed for dye removal from waste water. The utilization of solar UV and visible light for the degradation of various organic pollutants using semiconductor catalysts has drawn particular attention because it has been successfully employed to treat a wide range of toxic and non-degradable organic pollutants into readily biodegradable compounds in the wastewater without involving complex technologies. A variety of semiconductor catalysts, such as TiO_2, ZnO, Fe_2O_3 and CuO, are used as photocatalysts to degrade organic pollutants. CuO is a promising candidate because of its relatively low-cost. To enhance the photocatalytic ability of CuO for degradation of organic pollutants, H_2O_2 is often added because its electronic structure, characterized by a filled VB and an empty CB, plays an important role in the photocatalytic process. Some research reported in the absence of H_2O_2, CuO is not an effective photocatalyst for degrading organic pollutants because of its inability to produce a good amount of OH^- radicals, which have high oxidative ability and cause destructive oxidation of the organic dye. This result may be attributed to a fact that the VBs of CuO (Fig. 1.11) are more negative than the redox potential necessary for the generation of OH^- radicals. Thus, under illumination, CuO cannot create OH^- radicals and has a smaller amount of oxidative activities for degradation of organic pollutants.

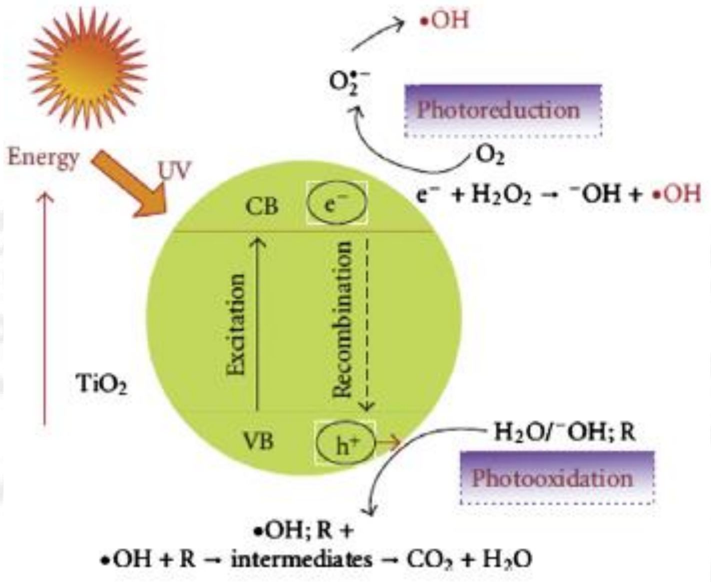

Figure 1.10 Schematic of the principle of photocatalysis [17].

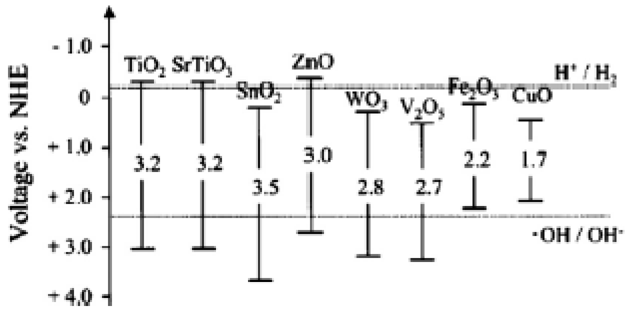

Figure 1.11 Diagram depicting the redox potentials of VB and CB as well as the band gap energies for various TMOs estimated at pH 7. The redox potential positions of H^+/H_2 and $OH^{\cdot}/OH^-$ at pH 7 are also illustrated [17].

1.4.6 **Antibacterial Activity** [17,23,24]

Although the decreasing particle size generally produces more toxic effects, the morphology of the CuO nanoparticles also has a very important function in the toxicity. Given the unique disposal of the surface features of the leaf-shaped particles, they were able to induce more surface-related phenomena. These particles generate more reactive oxygen species (ROS) on their surfaces, facilitating the higher toxicity of leaf-shaped particles compared with the other shaped particles, so, they can apply in antibacterial activity. Many researchs demonstrated that the potent antibacterial activity of TMOs nanoparticles is due to ROS generation by the nanoparticles attached to the bacterial cells, which in turn provokes an enhancement of the intracellular oxidative stress. This paradigm was confirmed by several assays including lipid peroxidation and reporter strains of oxidative stress. The established mechanistic route underlying the antibacterial activity of TMOs is depicted in Fig. 1.12, which clearly indicates that oxy radicals, namely superoxide anions, are generated in TMOs water suspensions [17,23,24].

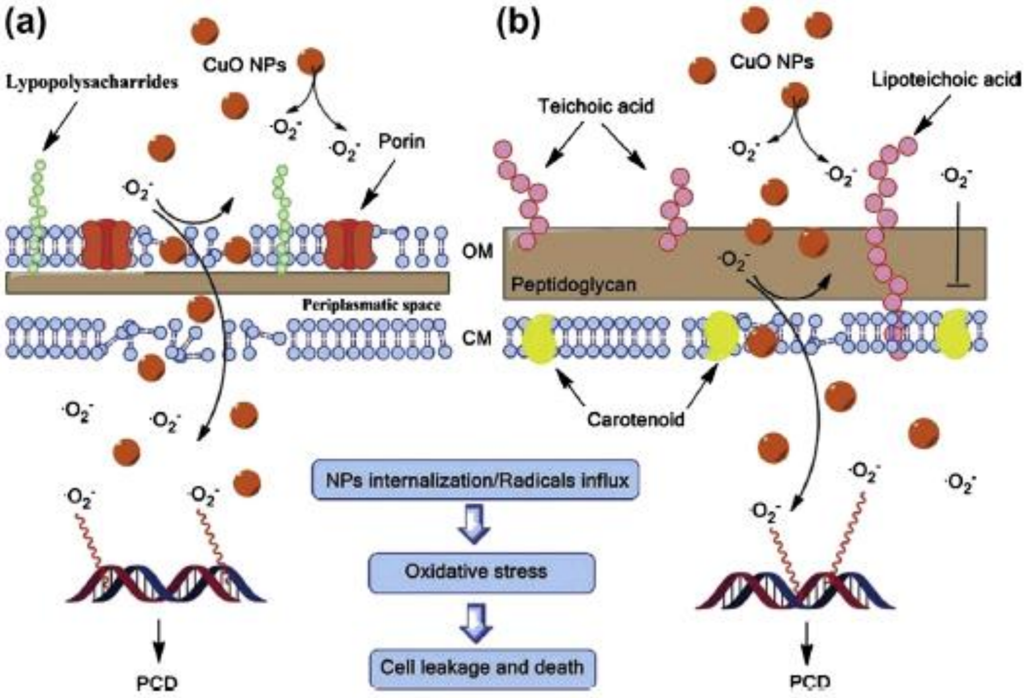

Figure 1.12 Schematic illustration of the antibacterial mechanism of CuO nanoparticles and the relative cellular structure of (a) Escherichia coli (Gram-negative) and (b) Staphylococcus aureus (Gram-positive) [17].

The antibacterial mechanism of CuO nanoparticles and the relative cellular structure of (a) Escherichia coli (Gram-negative) and (b) Staphylococcus aureus (Gram-positive) are showed in Fig. 1.12. The major structural differences between the two cells are the thickness of the rigid peptidoglycan layer and the presence of an outer membrane in Gram-negative cells. Gram-negative cells have a very thin peptidoglycan layer with only a few molecules thick, whereas Gram-positive cells have a very thick layer. The carotenoid pigments of S. aureus provide integrity to its cell membrane and increase its protection against oxidative stress. The bacterial cell damage is mediated by the harmful superoxide anions formed by the cell’s attached/ internalized CuO nanoparticles

1.5 Literature Review

Transition metal oxide nanostructures have drawn much research attention in recent year due to their properties and potential applications. There are a number of reports on the synthesis of transition metal oxide nanostructures as explained below.

In 2007, Chu *et al.* [25] reported the facile solvothermal method for synthesizing of Pb^{2+} doped ZnO nanodisks. The nanodisks have perfect hexagonal shape with about 1 mm in diameter and 100 nm in thickness. The existence of Pb^{2+} is vital to the formation of the disk morphology. Room temperature photoluminescence measurements showed two photoluminescence peaks centered at 518 and 648 nm.

Jiang *et al.* [26] synthesized CuO nanostructure via a facile hydrothermal method at different reaction condition using a nonionic surfactant polyethylene glycol (PEG) as the structure-directing template. SEM showed the various shapes of CuO nanostructures, including nanowires bundles. The morphology of the product was determined by the reaction temperature and time.

Zhang *et al.* [27] used simple wet chemical method for preparing different morphologies of ZnO nanorods. Zinc nitrate hexahydrate and ammonium hydroxide were used as the starting materials in the presence of polyethylene glycol (PEG, Mw=4000). Samples were characterized by XRD, EDS, TEM, SEM, ED and PL. The results prove the formation of ZnO with wurtzite structure. ZnO nanorods are single crystal and preferentially grow up along the [001] direction. The PL spectra showed that the ZnO nanorods have blue emission at 466 nm and green–yellow emission at 542 nm. The influence of reaction temperature, pH in system and activity of ammonia on the morphology has been investigated.

In 2008, Xie *et al.* [28] prepared ZnO whiskers with different sizes and hexagonal ZnO platelets by a simple route at low temperature (85 ^{o}C), using zinc chloride and sodium hydroxide as the reactants. The influence alcohol solvents on the morphology of the products was investigated. It is believed that interface-solvent interaction is responsible for the evolution of ZnO crystals.

In 2010, Shouli *et al.* [29] studied the effect of surfactant such as sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) and polyethylene glycol (PEG)- and calcination condition on the morphologies of 1D ZnO by hydrothermal method.

Hu *et al.* [30] fabricated ZnO nanostructure in ethanol solution of different alkali by surfactant-free solvothermal method. ZnO nanoparticles, nanowires and nanorods were obtained depending on the experimental conditions. The corresponding growth mechanism follows a typical self-assembly growth process. The effects of various alkalis on the structures, morphologies and properties of ZnO nanostructures were investigated. It is found that the surface defects should be responsible for the green emission observed in the as-prepared ZnO nanostructures.

In 2011, ZnO micro-flowers composed of hexagonal nanorods were successfully fabricated via soft chemical technique from zinc acetate dihydrate and sodium hydroxide by 1 h refluxing method by Wahab *et al.* [31]. The crystallinity of the grown product was analyzed by XRD, and the as-prepared micro-flowers have hexagonal wurzite structure by electron microscopy. Furthermore, the synthesized micro-flowers showed a better photocatalytic activity in the presence of methylene blue (MB) dye.

In 2012, Hassan *et al.* [32] reported the synthesis and characterization of novel CuO nanocrystals and their electrochemical and potential antibacterial activity. The utilized CuO nanocrystals were prepared by wet chemical method using copper acetate and hexamethylenetetramine (HMTA) as precursors. The physicochemical properties of the synthesized CuO nanocrystals having size ~6 nm were determined by XRD, TEM and UV-Vis spectroscopy. The antibacterial study was carried out by minimum inhibitory concentration (MIC) using E. coli as model organism. The TEM analysis reveals that CuO nanocrystals caused disturbance to the cell wall which led to the irreversible damage to the cell envelope eventually leading to the death the living cells.

Lu *et al.* [33] developed the routes for the fabrication of semiconducting nanomaterials with complementary conduction types should extend their potential use in a wide variety of industrial applications as well as expand research frontiers in 2012. Among the most promising nanomaterials, ZnO possesses several intriguing features that have attracted great interest for its use in nano-energy-related fields. Compared with unintentionally doped ZnO nanowires (NWs), which naturally possess stable electron-dominated conduction characteristics, it is difficult to incorporate acceptors into ZnO NWs and to ensure the stable conduction properties of p-type ZnO NWs. Herein, they review recent progress related to the synthesis and potential nano-energy applications of p-type ZnO NWs, highlighting their increasing role in semiconducting nanomaterials. Nevertheless, new strategies will have to be developed to overcome currently encountered problems in the synthesis of p-type ZnO NWs and, thereby, ensure the success of future ZnO-based industries.

In 2013, Suleiman *et al.* [5] successfully prepared copper (II) oxide (Cu=O) nanostructures with different sizes and shapes and their applied in different man daily life applications. They discuss different Cu=O nanostructures synthesis methods and their characterization as well as their applications. The pulsed wire explosion method of synthesis was discussed in detail. Then, Thaweesaeng *et al.* [34] synthesized pure ZnO and Cu - doped ZnO nanopowders (1, 2, 3, 4 and 5 wt% Cu) by coprecipitation method without further post-heat treatment. The results represented as-synthesized Cu-doped ZnO nanopowders in hexagonal wurtzite structure. All results indicated significant influence of Cu doping on relevant structural properties of ZnO.

In 2014, Moulahi *et al.* [11] prepared nanostructured hexagonal zinc oxide pills and words-like by hydrothermally synthesized using zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$) as an inorganic precursor and a dipic acid ($HOOC(CH_2)_4COOH$) as a structure directing agent. XRD studied demonstrated the existence of wurtzite ZnO of high degree of crystallinity with crystallite size in the range of 70–80 nm. The optical properties of the as-synthesized ZnO were investigated by UV–visible absorption and room temperature photoluminescence (RTPL). The band gap for ZnO nanorods and nanopills was found to be 3.25 and 3.27eV, respectively.

In case of the transition metal oxide (CuO and ZnO) on metal substrate, they have been reported, as shown below.

In 2005, highly oriented ZnO nanorods arrays with controlled diameter and length, narrow size distribution and high orientation consistency have been successfully prepared on ITO substrates at different growth temperatures by using a simple hydrothermal method. Guo *et al.* [35] reported the nanorods are high-quality single crystals growing along the [001] direction with a high consistent orientation perpendicular to the substrate. SEM images shown that the nanorods have average diameters of about 30–70nm by changing growth temperatures.

In 2006, Liu *et al.* [36] prepared different dimensional cupric oxide (CuO) nanocrystals and their architectures on copper foils via a hydrothermal process with the introduction of different types of surfactants including cationic surfactant cetyltrimethylammonium bromide (CTAB), anionic surfactant sodium dodecyl sulfate (SDS), nonionic surfactant poly(oxyethylene) (1,1,3,3-tetramethylbutyl) phenyl ether (Tx-100), ammonium peroxydisulfate (APS). The results show the products are pure monoclinic CuO. Series of experiments confirmed that the type of surfactants, the concentration of the surfactants, the concentration of the reactants and the reaction temperatures play the important roles in the morphology and nanoarchitecture of the products.

Peng *et al.* [37] were directly synthesized ZnO flower-like bunches on indium-doped tin oxide (ITO) glass substrates through a simple chemical bath deposition process. By adjusting precursor concentration, other morphologies (spindles and rods) were also achieved. It was revealed that both the inherent highly anisotropic structure of ZnO and the precursor concentration play the crucial roles in determining final morphologies of the products.

In 2007, Wang *et al.* [38] have been prepared ZnO whiskers arrays by a self-source procedure of the substrates. Zinc foils were used as substrates and zinc-ion source for direct growth of ZnO whiskers. They used a solution of alcohol and water (1:3, v/v), NaOH and CTAB as precursors. At 160 ^{o}C and 20 h, ZnO whiskers were synthesized. The as-prepared ZnO whiskers exhibited hexagonal prism-like shape showing well-defined crystallographic facets and hexagonal pyramid-like sharp tips.

In 2008, ZnO thin films assembled of ZnO nanostructured arrays have been fabricated on zinc substrates by a hydrothermal method. Yang *et al.* [39] were obtained ZnO thin films through the hydrothermal treatment of Zn foils at 60 ^{o}C in $NH_3{\cdot}H_2O$ solution and in the mixed solution of $NH_3{\cdot}H_2O$ and NaOH. Whereas ZnO thin films consisting of nanoflowers and corn-like nanorod arrays were obtained respectively in these solutions. Then, Li *et al.* [40] have been synthesized ZnO nanorod arrays with different morphologies on the zinc foils. The key influencing factors including the solution concentration of $Zn(NO_3)_2{\cdot}6H_2O$ and the lengths of reaction time are all studied and compared carefully.

In 2009, Gao *et al.* [41] were synthesized CuO nanoribbon arrays by a simple dehydration reaction for the first time. First step, $Cu(OH)_2$ nanoribbons were synthesized through the simple chemical route. Next, for the dehydration of $Cu(OH)_2$ nanostructures, the copper foils with the as-prepared $Cu(OH)_2$ nanostructures were heated at 50 ^{o}C for 12 h to remove moisture and subsequently at 180 ^{o}C for another 3 h to improve crystallization. The CuO products exhibited excellent hydrogen storage capacity and large BET surface area.

In 2011, Vanithakumari *et al.* [42] prepared CuO nanowires by heating Cu foils, rods and grids in ambient atmosphere without employing a catalyst or gas flow at temperatures ranging from 400 to 800 ^{o}C for 1-12 h. It was found that the nanowires were composed of CuO phase and the underlying film of Cu_2O. A systematic study was carried out to find the possibilities for the transformation of one phase to another with effectively.

In 2013, Wadati et al. [43] studied the electronic structures of solids, especially of transition-metal oxides by the photoemission spectroscopy, which is a powerful experimental technique. The hard X-ray photoemission spectroscopy (HXPES) has emerged as a more relevant experimental technique to obtain clear information about bulk states. Here, they describe how HXPES can be conveniently applied to study the interesting subjects on oxide thin films such as the composition dependence and the film thickness dependence of the electronic structures and the interfacial electronic structure of multilayers.

Mageshwari *et al.* [44] reported a facile and low-cost successive ionic layer adsorption and reaction method to synthesize nanocrystalline CuO thin films in 2013. Influence of deposition cycles on the physical properties of nanocrystalline CuO thin films was investigated. X-ray diffraction studies showed that all the films exhibit polycrystalline nature with monoclinic crystal structure. FTIR spectroscopy and Raman studies confirmed the formation of single phase CuO wherein the characteristic vibrational mode of Cu–O was identified. SEM studies revealed the formation of sporadic growth of rod-shaped elongated particles. Both the structural and surface properties of CuO thin films were improved with the increase in the deposition cycles as a result of which the optical absorption edge of CuO shift towards longer wavelength, and the optical band gap energy decreases from 2.48 eV to 2.31 eV. The room-temperature photoluminescence spectrum showed blue emission band centered at 468 nm, attributed to the near-band-edge emission of CuO due to Burstein–Moss effect.

In 2014, Ali et al. [45] were prepared ZnO doped SiO_2 thin films by the sol–gel method and annealed at different temperatures from 200 to 1100°C. SiO_2 matrix is selected as support due to their high flexibility, thermal stability and high porosity and surface areas. TEM images of ZnO synthesized nanoparticles are almost spherical with a relatively narrow size distribution in the range of 5–20 nm according to the annealing temperature. The newly prepared photocatalysts ZnO–SiO_2 films have been evaluated by the determination of their photonic efficiencies for degradation of methylene blue.

1.6 Research Objectives

1) To develop the synthesis of transition metal oxide, CuO and ZnO on metal plates.
2) To study the effect of pH of the precursor solutions, lengths of reaction times, and reaction temperatures on the morphology of transition metal oxide with nanostructures on metal plates.
3) To characterize the phase, morphology, atomic vibration, and optical properties of transition metal oxide on metal plates by XRD, SEM, TEM, FTIR and PL spectrometry.
4) To investigate some properties of the products such as antimicrobial activity against bacteria and photocatalysis.