Ministry of Higher Education and Scientific Research University of Baghdad Institute of Laser for Postgraduate Studies



Plasmon Resonant Enhancement of Photo catalytic Water Splitting Under Laser Illumination

A Thesis

Submitted to the Institute of Laser for Postgraduate Studies, University of Baghdad in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Laser/Physics

By

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_ أَلَتُهِ ٱلرَّحْزَ الرَّحِبَ

ٱقْرَأْ بِٱسْمِرَبِّكَ ٱلَّذِى خَلَقَ ٢ خَلَقَ ٱلْإِنسَنَمِنْ عَلَقَ ٢ ٱقْرَأْ وَرَبُّكَ ٱلْأَحْرَمُ ٢ ٱلَّذِى عَلَّمَ بِٱلْقَلَمِ ٢ عَلَّرَ ٱلْإِنْسَنَ مَالَمَ يَعْلَمُ ٢

صدق الله العظيم

سورةالعلق الايه (5)

Dedication

To my wonderful family (Mothers soul,

Father, Husband, Daughter, my Sun,

Brothers and Sisters)

who have raised me to be the person I am

today

Thank you for everything

Lina

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ABSTRACT

The demand of finding alternatives energy increased globally like photoelectrochemical cell. photoelectrochemical (PEC) of splitting water application, in storable hydrogen fuel by the direct use, becoming attractive technology nowadays.

This research consists of main steps to study the photocatalysis semiconductor. The first step is synthesis zinc oxide nanorod (ZNR) using chemical reduction method and hydrothermal method. The second step is fabricated graphene oxide (GO) by Hummer method to coat the ZNR catalysis by Electrostatic self-assembly method to form ZNR@Gr core shell. The third step deals with distribute Cu on ZNR and ZNR@Gr core shell sample to get ZNR/Cu core shell and ZNR@Gr/Cu core shell, as well as distribute Cu Ag on ZNR and ZNR@Gr core shell use reducing method. The final step is testing the efficiency and stability of the fabricated samples with different wavelength and different power (410, 473, 532, and 632) nm, (100, 200, 500, and 300) m W/cm⁻².

The morphologies and optical properties of all samples were examined by different techniques such as Field Emission Scanning Electron Microscope (FESEM), Transmission electron microscopy (TEM), Higher Transmission electron microscopy (HTEM), Atomic force microscopy (AFM), UV-Vis spectrophotometer, fluorescence spectroscopy (PL), and Zeta potential.

The ZNR@Gr/Cu Ag core- shell nanocomposites exhibit high absorption behavior in ultraviolet (UV) region of spectrum. In comparison with ZNR, the ZNR@Gr/Cu Ag core shell sample reveal superior absorption in the range 387– 1000 nm. The band gap reached to 1.2 eV for ZNR@Gr/Cu Ag core shell sample. Zeta potential surface charge for Cu and Cu Ag nanoparticles solution a stability in the data. This work used an electrochemical workstation EChem Startup Kits (ER461) from eDAQ compony. First all samples measured at Dark current density at 0 - 0.8 V versus Ag/AgCl scanning rate was 10 mV s⁻¹with 60 s for a cycle. The result suggested that there is an enhancement in conductivity occurs at ZNR@Gr/Cu Ag core shell catalysis reached to (1.2*10⁻²) mAcm⁻² compared with current density of ZNR (7.031* 10 ⁻⁵) mAcm⁻². Secondly, the samples measured at laser light with different wave length and power (410, 473, 532, and 632) nm, (100, 200, 500, and 300) mWcm⁻² respectively. Results showed that the photo current density increased at all wavelength of laser but the enhancement occurs at laser 410 nm especially with ZNR@Gr/Cu Ag core shell catalysis reached to 5.210 mAcm⁻². The ZNR@Gr/Cu Ag core shell catalysis also displayed enhanced PEC stability (95%), which prevented photo corrosion after 480 s, which show promising potential in the generation of H₂.

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|---|--|
| light 532nm illuminated | |

List of symbols and abbreviation

| | List | Unite |
|----------------|---|-------------------|
| h | Plank's constant | J.Sec |
| υ | Frequency | Hz |
| E _g | Energy gab | eV |
| H_2O_2 | hydrogen peroxide | |
| ОН | hydroxyl radicals | |
| a, b, c | Lattice constant | Angstroms |
| λ | Wavelength of laser | nm |
| Ι | Intensity transmitted | W/cm ² |
| I ₀ | the initial intensity | W/cm ² |
| С | the nanoparticles concentration per unit volume | Molarity |
| σ | extinction cross section | cm ² |
| X | the travelled distance | millimeter |
| t | Time | Minute |
| He-Ne | Helium–Neon laser | |
| Δx | The fringes spacing | millimeter |

| e | electron | |
|--------------|--|------------------|
| h+ | hole | |
| a | Absorption coefficient | cm ⁻¹ |
| PEC | Photo-electro-chemical | |
| ZNR | Zinc oxide nanorod arrays | |
| FTO | Fluorine-doped tin oxide | |
| ZNR@Gr | reduce graphene oxide at Zinc oxide nanorod arrays | |
| ZNR@Gr/Cu | reduce graphene oxide at Zinc oxide nanorod arrays doped by copper | |
| ZNR@Gr/Cu Ag | reduce graphene oxide at Zinc oxide nanorod arrays doped by copper and silver | |
| ZNR/Cu, | Zinc oxide nanorod arrays doped by copper | |
| ZNR/Cu Ag | Zinc oxide nanorod arrays doped by copper | |
| | and silver | |
| SPR | surface plasmon resonance | |
| GO | Graphene oxide | |
| ZnO | Zinc oxide | |
| СВ | The conduction band | |
| VB | The valance band | |

| NP | Nano particles | |
|------------|--|--|
| nm | nanometer | |
| 0D,1D, 2D, | Zero, One and, two dimensions | |
| NTs | nanotubes nano | |
| NRs | nanorods | |
| NWs | nanowires | |
| ZnO NPs | synthesis Zinc oxide nanorod | |
| AFM Atomic | Force Microscopy | |
| EDX | Energy dispersive X-ray | |
| PL | Photoluminescence spectroscopy | |
| UV VIS | UV-visible Spectroscopy | |
| TEM | Transmission Electron Microscopy | |
| FE-SEM | Field Emission Scanning Electron Microscopy | |
| HTEM | Higher Transmission electron microscopy | |
| НМТА | hexamethylenetetramine | |
| APTM | amino-propyl trimethoxy silane | |
| PVA | Polyvinyl alcohol | |
| η | Efficiency of catalysis | |

| Ι | Photo current density | mA cm- ² |
|---------------------|-----------------------------|----------------------|
| ${ m J}_{ m light}$ | Intensity of incident laser | m W cm ⁻² |

Chapter One

Introduction and Basic Concepts

1.1 Introduction

The great important humanity troubles, that is the increase of needing economic energy for a long-term. Energy obtainment from light has attracted huge interesting for its very good potential owing to low-cost and clean hydrogen production. [1]

Photoelectrochemical (PEC) production of hydrogen is the favorable technologies that can enhance potential function, a cost and clean. The conception of Photoelectrochemical water splitting for production of hydrogen was been realized, with first manifestation in by Fujishima and Honda. [2,3]

The water splitting of PEC is good technique, but it is complicated process because the semiconductor system should produce enough voltage during irradiation for splitting water, the band gap of photo catalysis or work electrode should be sufficiently small to absorb a more part of the light spectrum, the system must display stability contra corrosion in aqueous electrolytes, at the surfaces the potentials of band edge must mount the oxygen and hydrogen redox potentials. [4-6]

There are many strategies have been achieved to conquer these problems of water splitting of PEC. First, by changing the nanomaterials morphology to improve the activity surface area of the photocatalysis. Second, the hybridization of two or more different material was carried out by forming to enhance the separation of charge, widening the absorption of light and improving the electrode surface area. Third doped the semiconductors with different metal and nonmetal nano particle to reduce this difficulty to get surface plasmon resonant enhancement.

This research has been mixed between these strategies by synthesizing Zinc oxide nanorod arrays (ZNR) on Fluorine-doped tin oxide (FTO) substrate, then covered by five layers from reduce graphene oxide (ZNR@Gr core-shell), then doped ZnO nanostructures with different metal nano powder Cu and Cu Ag (10-15 nm) to get (ZNR@Gr/Cu core-shell, ZNR@Gr/Cu Ag core-shell, ZNR/Cu core-shell, ZNR/Cu Ag core-shell) thin films to improve the catalysis properties.

Finally used surface plasmon resonance (SPR) to improve the ability of the absorption of the photo catalysis, all the thin films or photo catalysis and (SPR) proved synergistic improvement in photoelectrochemical water splitting activity.

Zinc oxide semiconductor materials, has great attention because it is nontoxicity, low cost and controllable morphology. It is the large band gap (3.37eV), and high recombination of photoexcited electron hole pairs, restricted conductivity of charge, but the observation, synthesizing composites on morphology with mixing with other nanomaterials was proved to be a beneficial photo catalysis. [7,8]

Graphene oxide (GO) can prove to be remarkable material to enhance the absorption of ZNR photo catalysis because of GO has very good electrical conductivity, high surface area and it is absorption at the IR regain of light spectrum, it was worth studying the graphene advantages contacting, coating and doped by metal nanoparticle decoration as (Cu, Ag, Au, Pt, Al.... etc.) on the ZNR surface. [9,10]

Surface Plasmons resonance (SPR) is optical attribute of metallic nanostructures. It includes a collectivized vibration of conductivity electrons excited by the electromagnetic field. The optical properties are greatly improved when the particle size of a metallic material can be decreased to the few nano meter range, and its behavior results exactly changing than the bulk metal one. [7] [11,12]

1.2 Photoelectrochemical (PEC) of Water Splitting

Photoelectrochemical cell is expected to have a favorable future to replace fossil fuels by using energy of light to split water $(2H_2O \rightarrow 2H_2+O_2)$ for the production of hydrogen. Solar light has been used to split water using a perfectly clean and friendly environmentally method. [13,14]

A three-electrode arrangement of PEC cell have been applied in the measurements of photocatalytic water splitting, as explained in fig. (1.1) A semiconductor can be utilized as a photo anode or photo catalysis and a platinum foil can be applied as a counter electrode, KCl or Ag/AgCl saturated electrode can be applied as a reference. [15]

Zinc oxide is the favorable materials for an active solar cell, it has high carrier mobility, very good crystallinity, and a high surface area, very good supply a geometry of light absorption and electrolyte transportation. However, the solar to hydrogen conversion activity obtained by Zinc oxide as yet is a weak for its large band gap that absorbs at UV light region. Metal oxide films synthesized on Fluorine Tin Oxide (FTO) or Indium Tin Oxide (ITO) glass substrate can be used as the photoanode. [16-18]

The unique laser light source has specific properties such as high intensity, monochromaticity, and low beam divergence. Huge attention to use laser beams as an excitation source to study the photocatalysts efficiency, because the conventional lamp could cause several problems such as emitting over broad spectral wavelength. Metal oxide nanomaterials can be applied as photoelectrode for PEC water splitting because their relatively high surface area, and low cost. [19]



Figure (1.1) A diagram explaining a PEC cell with a standard three-electrode arrangement. [15]

1.3 Photocatalysis

Photocatalysis is the photoreaction acceleration by the action of a catalyst. ZnO photocatalyst nanostructured has been promising researched due to its use in water photolysis of electrochemical for production of hydrogen. Hydrogen is an effective renewable energy and clean source to fossil fuels. [20]

The band gaps and conduction band, valance band positions for many selected semiconductors are given in fig (1.2) interfacial charge transfer occurs when the charge carriers are travel between the photocatalyst surface and the adsorbed chemical species.

The excellent transfer of electron tack place, the decrease potential, and adsorbed acceptor species must be lower than the conduction band (CB) position. To occur transfer hole, oxidation potential of the absorbed donor species should be higher than the valence band (VB) position. [21-22]



Figure (1.2): The semiconductors Band edge positions with the aqueous electrolyte at pH = 0 [22]

When the energy of photon (hu) is higher than the Photocatalytic applications band gap energy, it can be excited an electron from the valance band to the conductive band, that way, generating an electron e and appositive hole h+, in the CB and, alternately. [23,24]

Both electron e and hole h+ transfer to the surface of catalyst to combine again or prefer are do interaction with synthesis absorbed on the catalyst. The incorporation of the positive hole h+ with water and/or hydrogen peroxide H₂O₂ produce hydroxyl radicals OH·, strong oxidants that oxidize the organic composite in the photo catalytic surface. At the same time, oxygen molecules absorbed on the photocatalyst can be decreased by the electrons in the CB as shown in fig (1.3).[25]



Figure (1.3) the photo catalyst of TiO₂. [25]

When illumination of photocatalysts by light, the processes in photocatalytic generation of hydrogen accrues, the photo excited electrons and holes can be occurred at the CB and VB, alternately. It can be travelled to the counter electrode superficies, meantime the photogenerated holes can be travelled to the photocatalysts surface. [26]

Redox reactions occur at the surfaces of electrode when separated electrons and holes tack place with (electron acceptors) in the electrolyte to produce oxygen and hydrogen. The CB electrons can migrate from the implied substrate to compass the counter electrode, platinum foil, to split the water to h_2 gas, as display in Equation (1.1). Semiconductor photocatalyst n-type, the holes at the VB generated by band gap excitation of the catalyst can move to the superficies of electrode to oxidize water (Equation 1.2). [26,27]

$$4H+(aq) +4e \rightarrow 2H_2(gas) -----(1.1)$$

$$4h++H_2O(aq) \rightarrow O_2(gas)+4H+(aq) -----(1.2)$$

1.3.1 Enhance the Efficiency of Photocatalysis

The efficiency of photocatalytic depends on surface of catalysis (measured as the reactions number that occur per unit time and area) have been respected on the absorption process of light that controls the active holes number / electrons in the material. [28]

The absorption intake has been enhanced by increasing the specific catalysts surface area. Modulation to semiconductor surfaces such as addition of metallic and nonmetallic NP, incorporation with other semiconductors is useful in decreasing the recombination rate of electron and hole and thereby rising photocatalytic process activity. Fig (1.4) shows the metallic nano particle decorated with semiconductor. [29,30]

Transition metal or nonmetal could add new levels of energy as electron acceptors, and substantially enhanced the visible light absorption semiconductors ability. [31-33]



Figure (1.4) shows the metallic nano particle decorated with semiconductor and illuminated by visible light.[28]

The two photocatalysts of semiconductor enhanced an excellent to increase the photocatalytic activity by improving the charge separation, and increasing the photoexcitation range of energy for the system. There are three types of coupled semiconductor photocatalysts depending on the several composite semiconductors band gaps, which are type one with a straddling gap, type two with a staggered gap, and type three with a broken gap as shown in Fig (1.5). [28] [34]



Figure (1.5). The three several photocatalysts types (a) type-I, (b) type-II, and (c) type-III. [34].

As for the type one, with a straddling gap during the irradiation, Photoexcited electrons gathered in semiconductor B and photoexcited holes accumulated in semiconductor A due to interfacial electron transfer. Not only is light absorption enhanced in the that photosystem, but also the separation of electron hole, which can be improved by the interfacial transfer of charge in the composite. [35]

Type two, the semiconductor B (VB) and (CB) are lower than semiconductor A, thus the photoelectrons generated can travel from the semiconductor A (CB) to that of semiconductor B and the corresponding holes in the semiconductor B (VB) can migrate to semiconductor A with a lower decrease potential, and a lower oxidation potential, thus electron hole pairs a spatial separation will be completed. Type three, there is no electrons and holes transmission between B and A semiconductor. [34-36]

graphene material has exceptional physical properties, containing excellent charge transport activity, unrivaled optical properties, high thermal conductivity, large surface area, and well mechanical strength, a huge of attempts was achieved to connect the graphene with different semiconductors to enhance their photocatalytic efficiency. [37,38]

Metallic and nonmetallic NPs display efficiency that will be enhanced upon light illumination to excite surface plasmon resonant (SPR). In addition to the widely increased applied of (SPR) in photocatalysis can be improved the photocatalytic in transition metal - oxides by metallic NPs combination. [39]

SPR have proved their capabilities to enhance the activity of the photocatalysis. It is attention reminding that a mediate enhancement of catalytic activity applying (SPR) because of the temperature rise resulted by absorption of light. [29]

Nanofibrous, nanorod, nanowire, nanobelts, and nanotubes photocatalysts were hugely studied for their individual long aspect ratio, large surface area, and being simply functionalized, different strategies had been developed to synthesize the materials with different morphology by, the hydrothermal method. [40,41]

1.4 Nanomaterials

The fundamental of nanoscience and nanotechnology are nanoscale materials which located as a collection of materials where at least one dimension is less than 100 nanometers. Nanotechnology deals with tiny structures. The applications in different types of nanomaterials based on their physical properties, high surface area and small volume and predictable to have a broad range in multiple fields such as optical communications, electronics, and biological systems as shown in fig (1.6). [43]



Figure (1.6) Different applications of Nanotechnology. [44]

Two types methods to synthesize nanomaterials Top Down and Bottom-Up process as shown in fig (1.7) Top-Down approach mainly involves the physical processes for nanomaterials synthesis.

This type can make nanomaterials in large quantities but with less control on the size, shape and uniformity in composition. Bottom-Up mainly involves colloidal chemical synthesis methods and self-assembly. This type can produce nanomaterials with uniform compositions and controlled size/shapes although the yield of such a reaction is relatively low. [45]



Figure (1.7) Schematic showing Nanostructure synthesis approaches with classifications. [44]

The nanomaterials structure can be categorized by their dimensions. Fibers, nanotubes, and nanorods are the one-dimensional nanostructures. At the nano scale the physical properties change while when the same material at bulk scale. The percentage of surface atoms increase in smaller particles and this increase, leading to change in chemical and the materials physical behavior. Due to their substantial applications in materials technologies including optics of nanodevices, electronics, and analytical technologies. [46-48]

There are three different types nanostructures of nanomaterials: zero dimensional, one-dimensional and two-dimensional nanostructures. OD nanostructures have been called as nano-particles (NP) with the probable morphology of spheres and dots., one-dimensional nano-structures are usually named by a several of names inclusive nanotubes (NTs), nanorods (NRs), nano

whiskers, nano-wires (NWs), and nano fibers. Meanwhile 2D nanostructures have been named as some nanoplatelets and thin films. [49]

The nanomaterials dimensions range are about different nanometers to 100 nm. It is significant to observe that the variation the nanomaterials size and dimensionality lead to in a change in electronic structures and the materials structural characteristics. [50]

1.4.1Metal Oxide Semiconductors

Metal oxides are a chemical compound formed between metals, such as Na, Zn, Li, etc., and oxygen. It was classified in to a conductor, an insulator and a semiconductor. For a conductor, the VB and the CB are slightly loaded by electrons, the energy band gap of material more than 4 eV, it has been categorized as an insulator, and when band gap energy will be transcended by optical and thermal excitations to make electron hole pairs in the CB and VB this material is assorted as a semiconductor. A reduce in an oxide particle average size will be changed the band gap magnitude, with intense influence in the chemical reactivity. [51-52]

Metal oxide was played huge attention from researchers in many branches such as physics, materials science and chemistry. The metal oxides nanostructured properties can be led to the enormous applications as storage of energy, photocatalysts for environmental processes, solar cells, and hydrogen production by water photolysis. [53-57]

1.5 Zinc Oxide (ZnO)

Zinc oxide is a white powder, but in nature it appears as the rare mineral zincite, which usually includes manganese and other impurities that change color from a yellow to red. ZnO crystallizes in two major forms, hexagonal wurtzite and cubic zincblende. Wurtzite structure has stabled structure and it is the most a
hexagonal structure with lattice parameters c = 0.520 nm and a = b=0.3296 nm. [58]

The zincblende form will be settled by forming ZnO on underlying with cubic lattice structure. ZnO changes to the rocksalt at high pressures about 10 GPa. ZnO structure is classified as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions form will be settled by forming ZnO on substrates with cubic lattice structure as shown in fig (1.8). [59]



Figure (1.8) Zinc oxide unit cell in (a) rocksalt, (b) zincblende and (c) wurtzite structures of crystal [61]

ZnO has large band gup 3.37 eV, and a high energy of 60 m eV, the optical absorption is bounded to the UV region. In order to obtain wide band photo response in the Vis - region, Pt, Au, Ag, Al, Cu, Ni, nanoparticles structures must be deposited on ZnO semiconductor with accuracy of domination on size and distribution [60,61].

ZnO can be chosen as photocatalyst because of its high activity of catalytic, not expensive material, and non-toxic nature. Regrettably, but it is not highly active under visible light irradiation due to the large band gap of it. A mean problem in ZnO photocatalyst is instability of watery sol. for photo corrosion upon UV illumination. Many reported was combination of Ag- NPs onto ZnO films to an enhances of photo-catalytic activity and higher ZnO stability stopping the photo corrosion. [62-64]

The modification of ZnO by decorated with some elements, e.g., Au, Cd, Ag, Pd, Co; coupling with other metal oxides, e.g., WO₃, SiO₂, and CuO to decreases the energy band gap and to stretch the visible absorbance light and also, for electron- hole separation and increasing a photocatalyst efficiency. [65] The level of energy and electron transition upon illumination by visible light of undoped and doped ZnO could show in fig (1.9)



Figure (1.9) The energy level and electron transition of ZnO undoped and doped up on illumination with visible light [66]

1.5.2 Synthesis of ZnO Nanostructures

Morphologically, ZnO is a very attractive material, because zinc oxide can be grown in an ample verily of nanostructures. Different chemical and physical way were suggested to synthesize zinc oxide nanostructures by governing the conditions of experimental. [67]

Several fabricates of ZnO nanostructures, for example nanowires, nanoribbons/nanobelts, nano rings, nano castle, nanospheres, nanofibers, nanorod and heterostructures so on. In addition, some of these morphologies are presented in fig (1.10) and fig (1.11) refers to Techniques for the synthesis of ZnO NPs. [65,68-71]



Figure (1.10) ZnO morphology, nanospheres, nanorods, nanobelts, nanoplates, tetrapod and multipedes. [65]



Figure (1.11) ZnO NPs synthesis Techniques. [68-71]

1.5.2.1Chemical Methods

There are many chemical methods to synthesis ZnO NPs such as sol-gel method, solvothermal method, chemical vapor deposition method, microemulsion, and Hydrothermal method.

Nevertheless, recently a new synthesis method has been introduced and that is called biosynthesis scheme in which the NPs are prepared by using biological materials having significant reducing and stabilizing features. Moreover, NPs with variable size and shape can be achieved through this process. [72]

Chemical methods are expansive and have many disadvantages the synthesis process, separation, and nanoparticles purification from surfactants, organic solvents, co-surfactants, and toxic materials, which involve use of toxic. Biological processes and green chemistry have led to the rapid enhancement, ecofriendly and cost-effective biosynthesis of zinc oxide Nanorod. [72-75]

1.5.2.2 Hydrothermal Method

A chemical interaction in the subsistence of watery solvents more than 100°C and at pressures more than 1 atm is called Hydrothermal method. It is solution method which is vastly used for the ZnO NPs fabrication. A Teflon lined stainless steel autoclave has been used like the thermal reactor, Since the interaction cavity has been locked and heated, a high pressure can be created in the cavity and thus results in the synthesis of good crystalline ZnO NPs. [75,77]

Hydrothermal assembly method is finding rising applications in solidstate chemistry and science of materials. It is a significant method for crystal outgrowth and the formed of novel materials with good characteristic. [78-79]

There are some key of parameters to control the crystallinity and morphology of the synthesized ZnO NPs such as concentration, pH, temperature, pressure seeding conditions and duration time of hydrothermal reaction. When changing these parameters, the results showed that a different of ZnO NPs, including nano towers (NTs), nano rods, (NRs), nanoflowers, nano wires, and nanoplate. [80,81]

Hydrothermal method has been included some advantage such as reduces nanoparticles agglomeration, simple procedure, good control on the morphology, occurs without any high temperature recurred. [82,83]

1.6 Graphene Nanomaterials

Graphene word has been created from the Greek word "Graphein" that means to write. Graphene has a one atom thick planar nanosheet of sp²-bonded carbon atoms filled in a honeycomb lattice or a layered structure or multi coats of carbon atoms that are violently filled into benzene rings extracted of their atoms of hydrogen. Graphene is a morphology origin of all bounds of carbon containing graphite, carbon fibers, nanobuds, nanoring's, single walled or multiwalled carbon nanotubes. [84-86]

The different functionalized NPs, chemically stable metal NPs (e.g., Au, Ag, Ni, Pt, Pd and Cu) NPs, metal oxides NPs (e.g., alumina, silica, zirconia, Titania), metal carbides (e.g., SiC) have been used to enhance the physical properties and electrical conductivity of graphene hybrids for different fields of application. [86-88]

1.6.1 Graphene oxide (GO)

Graphene has been a 2D material. It is the oxidized graphene form, with O active groups decorated the sp² C main plane. All physical characteristic of graphene was matched GO, those of graphene by easily ejecting the feasible groups from its surface. Because of the subsistence of the O active groups, graphene oxide is as well hydrophilic and it could be sprinkled in water solution,

inverse to graphene which is hydrophobic. The GO flakes size ranges from a few nm to mm. [89-91]

GO has structure of non-oxidized essential speck of changeable size, which can be detached from each other by aliphatic six coterie including hydroxyl groups, epoxide groups, and dual bonds [76]as fig. (1.12).



Figure (1.12). Graphene oxide chemical structure. [93]

1.6.2 Graphene oxide Synthesis

Hummers method is the excellent common way for creating graphite oxide, that graphite is patronizing with a blend of sodium nitrate, sulphuric acid and potassium permanganate. Graphene oxide is effectively a byproduct of this oxidization as the interplanar spacing between the graphite layers is increased when the oxidizing agents react with graphite, [92,93]

The completely oxidized compound will then be dispersed in a base solution such as water, and graphene oxide is then produced. Graphene oxide includes monolayer flakes and some layers graphene, punctuate it with water (according on the basal middle, the sheet-to-sheet reaction will be softened by functionality of surface, it causes to enhance hydrophilicity). [94-96]

The fabrication of GO an attractive material in several fields: electronics transparent conductive films and sensors, composites materials, medicine, biology and clean energy devices. An ideal Graphene oxide appeared as brownish solution, whose transparency and it can be tuned by differing the solute concentration. [97-111]

1.6.3 Graphene Properties

The wonderful graphene properties are the interest great areas, each of which appears to be excellent to contender materials. This material prides an excess of matchless properties that consisted Graphene is strong material, which is over 300 times higher than steel. [87]

It has high thermal and electrical conductivity, the capability to suffer high electric current densities, very elastic, readily chemically functionalized making the material very multilateral and permitting graphene to be inserted into a range of devices and materials to befit the purposed application. [102-104]

High-surface area of graphene a single layer has been applied to create electrodes for future different application such as sensing and catalysis applications. [105-106]

1.6.4 Application of Graphene

graphene was incorporation of properties required for several applications, creating new products. Analysis of novel layered materials. Numerous, trustworthy, safe, graphene-related nano material synthesis large scale production, that will fulfill the needs of several areas for applications. [107-108]

Ways and protocols to get graphene-related nano material synthesisbased components and structures into systems that will enhance new functionalities and application.

New connotation for integration of the graphene related nano material synthesis in existing technology program for flexible electronics and energy applications. Fig. (1.13) shows different application of graphene. [109-110]



Figure (1.13) scheme of applications of graphene in different fields. [110]

1.7 Surface plasmon resonant (SPR) in NPs

Surface plasmon resonant (SPR) is an interaction between light electromagnetic field and the matter. The physical interpretation of (SPR), is a

metallic nano particle has been explained as ionic cores a lattice with conduction electron. When the particle has been illuminated, the light electromagnetic field complied these electrons of conduction traveling them at the nano particle surface. [111]

These electrons have been bounded inside the nano particles, positive charge can be amassed in one side while negative charge in the obverse side, then producing an electric dipole, this dipole will be created the electric field inside the nanoparticles opposite to light that will force the electrons to return to the equilibrium position as shown in fig. (1.14). [112]

The behavior is like to a linear oscillator and a returning force proportion to the displacement from the equilibrium position. When the field is closed, they can oscillate with a confirmed frequency that is named the resonant frequency; or plasmonic frequency. [113]



Figure (1.14). The light interaction with a metallic. [48]

Fig. (1.15) display the absorption wavelength and the extinction cross section with ten nm size metallic nano particle synthesis. It is located that with noble metal nano particles the extinction cross section will be up to ten times

their geometrical section; It is worth noting that the light absorption is an exponential credence on the absorption cross section being I_0 the initial intensity, C the nanoparticles concentration per unit volume, E their extinction cross section and x the distance as shown in equation (1.3). Therefore, average growing in the extinction cross section will resulted to a great improvement of light resonance. [48]



Figure (1.15) Absorption wavelength and extinction cross section of metallic nano particles. [48]

 $I_{(x)=}$ $I_{0.e}^{-CE.X}$ ------ (1.3)

A material of metallic have a continuous spectrum overlap of (VB) and CB of obtainable states, some inside levels do not split suffice to overlap these bands therefore the system may offer inter band like of transitions to those in semiconductors. SPR individual, since the values of cross section located here are larger than other optical processes like electronic transitions in semiconductors, weakness concerning absorption process in solid, or electronic excitations in molecules a direct ideal of the grate extinction in metallic nano material synthesis because of SPR excitation is supplied by a rapprochement with inter band transitions. [115-114]

1.8 Literature Survey

H.L. Jiang. et al. in 2011 [116] Au@Ag core-shell nano material synthesis freeze on a metal organic framework (MOF) by an alternate deposition reduction method. Studies of catalytic display an excellent bimetallic synergistic effect of core shell structured Au@Ag nano material synthesis, which have much higher catalytic efficiency than monometallic nano material synthesis.

B. Li. et al. in 2012 [117] an excellent-achievement ZnO/grapheneoxide (ZnO/GO) NPs photocatalyst can fabricated by a facile chemical deposition way and applied for the organic dye photodegradation from water under visible light, ZnO/GO NPs displayed uncommonly improved photocatalytic activity than GO- sheets and flower-like ZnO particles.

F. Han. et al. in 2014 [118] A hybrid structure of reduced graphene oxide (rGO) sheets/ZnO nanorods was prepared and its photoluminescence intensity ratio between the UV and defect emission was enhanced up to 14 times. By controlling the reduction degree of rGO on the surface of ZnO nanorods, the UV emission was tuned with the introduction of localized surface plasmons resonance of rGO sheets. The suppression of the defect emission was ascribed to the charge transfer and decreased with the distance between the rGO and ZnO nanorods.

A. Alshanableh. et al. in 2016 [119] This work demonstrated a novel crystal growth of ZnO and formed in a low temperature (90 °C). It is intensively studied for the highly crystalline nanostructures synthesis by two-step facile hydrothermal and air-cooled hydrolysis method which tuned zinc oxide nanostructure from single nanorod to twin nanotube.

Sh. Allami et al. in 2017 [120] A branched-nanowire of ZnO (BNW) photoanode can be doped with N photoelectrochemical cell (PEC) to generateH₂. The photoanode can be demonstrated in photoelectrochemical at different power

densities under both illuminated and dark conditions. Increasing the N amount in the ZnOBNWs increased the photocurrent in the PEC.

J. Albero. et al. in 2019 [121] The graphene photocatalytic activity derives from defects formed during synthesis. It can be offered that the defects introduction in the graphemic lattice add to the small nanoparticles of metal oxide amounts incorporation on the surface of graphene improves the graphene photocatalytic efficiency. These two properties strong doping, and crystal orientation have been enhanced the photocatalytic efficiency in graphene-based materials for water splitting.

S. Hejazia. et al. in 2019 [122] Synthesis Cu-decorated TiO_2 nano-tubes by self-organizing anodization of Ti–Cu (TiNTs) Cu concentration of 1.5. Under illumination UV light the Cu²⁺ ion-decorated TiO₂will be changed to nano-tubes on top of the TiNTs. The resulting of Cu decorated TiNTs have been a strongly improved photocatalytic efficiency for H₂ generation.

Also, F. Shi et al. in 2019 [123] Induced of plasmon hot electrons improvement method to enhance Oxygen reduction reaction (ORR) (Ag)silver - based electrocatalysts property. Using graphene in this work and Ag nanoparticles, by tuning laser power and the absorption positions, due to properties Ag catalysts was improvement.

U. Baig et al. in 2020 [124] Used pulsed laser ablation to synthesize in liquid visible-light-functional NiO graphitic carbon nitride (NiO@g-CN) for work in photoelectrochemical water splitting as a photoanode interaction with a solar simulator. Founding improvement in density of photocurrent under visible light, and the band gap estimation showed the band gap energy reduced and improvement in the visible-light resonant, and reduction of the recombination of photo-excited electron hole pairs.

Also, Xi. Hu et al. in 2020 [125] (α -Fe₂O₃), is most excellent materials of photoanode, shows localized low carrier conduction, small carrier transport. the carbon quantum dots (CQDs) photothermal effect is put in the photo electro chemical cell water splitting process enhanced the efficiency of the photo catalysis. Upon near IR light irradiation, the CQDs/Fe₂O₃/TiO₂ photoanode temperature can be raised. Cobalt-phosphate (Co-Pi) is introduced on the surface of the photoanodes for acting as an oxygen evolution. enhancing a unique platform to benefit on the photo-thermal properties to increase the photo electro chemical cell photoelectrodes efficiency.

1.9 Aim of study

Increasing the efficiency of Photo catalytic Water Splitting for zinc oxide by enhancement physical absorption using Nano- composite material with laser Illumination at different wavelength (410,473,532,632) nm and different power density (100, 200,300,500) m W cm $^{-2}$.

Chapter Two

Experimental set up and procedures

2.1 Introduction

This chapter includes all the experimental procedures which have been done involving the chemical materials utilized, synthesis of ZNR, ZNR@Gr core -shell, ZNR/Cu core -shell, ZNR/Cu Ag core -shell, ZNR@Gr/Cu core -shell and ZNR@Gr/Cu Ag core -shell nanostructure thin films, procedures, parameters effect and characterization devices. Finally, the photocatalytic water splitting by illuminating under laser light with different wavelength (410,473,532,632) nm and different power density (100,200, 500, 300) m Wcm⁻².

2.2 Procedure

2.2.1 Synthesis ZnO nanorod (ZNR) Catalysis

The materials and device applied in this work can be exhibited in table (2.1)

Table (2.1): The chemical characteristics of materials and device applied to form ZNR.

| No | Chemical - material | Chemical - formula | Molecula r Weight (g/mol) | Purity % | Physical form | Purveyor |
|----|-----------------------------------|-----------------------------------|---------------------------------|--|--|----------------------------------|
| 1 | Hexamethylenetet ramine | (CH ₂)6N ₄ | 140.19 | 99% | White powder | New Delhi- 110002 INDIA |
| 2 | Zinc - nitrate | $Zn (NO_3)^2.6H_2O$ | 297.47 | 98% | White powder | Shanghai, China |
| 3 | Fluorine-doped tin oxide (FTO) | | | | Glass sheet (electrical connector) | UK |
| 4 | Ethanol absolute (EtOH) | C ₂ H ₅ OH | 46.07 | 99.9 | Transparen t liquid | Schar lab S.L. Spain |
| 5 | Acetone | C ₃ H ₆ O | 58.08 | 99.9 | Transparen t liquid | Sigma Aldrich |
| 6 | Spinner coating | | | | plastic | Computer van |
| 7 | Oven Jrad | | | | Steles steal | Syria |
| 8 | Autoclave | | | | Steles steal | China |
| 9 | Deionized Water | H ₂ O | | high degree of purity of addition al ions | Transparen t without color | Iraq |
| 10 | Ultrasonic | | | | Steles steal | China |

The ZNR have been synthesized due to the work of other researchers [127] with some modification in two method (chemical reduction method then hydrothermal method). Step one the (fluorine-doped tin oxide) FTO substrates were washed with 50 ml of deionized water, ethanol 25 ml, mixed with 25ml acetone for 20 min at 90 C° at an ultrasonic bath. Then, ten drizzle from hexamethylenetetramine (HMTA, 0.5 M) and ten drops of Zn (NO₃)² solution, (0.5 M) were alternately distilled onto the substrate (FTO).

Next interacting for 10 minutes, the sol on (FTO, $2 \times 3 \text{ cm}^2$) substrates can be distributed evenly by using a spinner coating, the FTO was heated at 200 C° for 20 min by Oven Jrad. To be sure that the seeds are formed on the substrate all above process should be repeated for 3 times (chemical reduction method). Then the second step the samples of ZnO nano seeds substrates were immersed in the mixed of 0.05 M from HMTA and Zn (NO₃)² solution then stood up right into stainless-steel autoclave at 122 C° for 4h then two days at room temperature. Then, all the samples were cleaned by deionized water then heated at 100 C° for 4 h (hydrothermal method) .as displayed in fig. (2.1).



Figure. (2.1). The steps of ZNR synthesizes.

2.2.2 Synthesis of Graphene Coated ZNR (ZNR@Gr core -shell) Catalysis

The synthesis ZNR@Gr core-shell was done by two stapes A. preparation graphene oxide by hummers method then B. Synthesis ZNR@Gr core-shell.

The materials and device used are shown in table (2.2).

Table (2.2): The chemical materials and device characteristics applied to form ZNR@Gr core-shell.

| No | Chemical material | Chemical | Molecula | Purity % | Physical | Purveyo |
|----|-------------------|-------------------|---------------------------|------------------|---------------|----------|
| | | - formula | r Weight | | form | r |
| | | | (g/mol) | | | |
| 1 | Graphene platelet | | | 99% | black powder | sky |
| | nano powder | | | | 15 nm | spring |
| | | | | | | TX.7708 |
| | | | | | | 2.USA |
| 2 | Sulfuric acid | H_2So_4 | 98.08 | 98% | without color | LOBA - |
| | | | | | | Chemie |
| 3 | Sodium nitrate | NaNO ₃ | 84.9947 | 99.5 % | Transparent | Sigma- |
| | | | | | crystalline | Aldrich |
| | | | | | without color | |
| 4 | Potassium, | KMnO ₄ | 126.035 | 98% | Green | Sigma- |
| | oxide(oxo)mangane | | | | colored and | Aldrich |
| | se | | | | darkening | |
| _ | | | | | with time | |
| 5 | Hydrochloric Acid | HCI | 36.46 | | Transparent | Fluka |
| | | | a 4 a 4 4 - | | without color | ~ . |
| 6 | Hydrogen peroxide | H_2O_2 | 34.0147 | | Transparent | Sigma- |
| _ | | | | | without color | Aldrich |
| 7 | Oven Jrad | | | | Steles steal | Syria |
| 8 | Deionized Water | H_2O | | high degree | Transparent | Iraq |
| | | | | of purity | without color | |
| | | | | -empty | | |
| | | | | 0I additional | | |
| | | | | iona | | |
| 0 | Amino propyl | C.H.3NO. | 221 272 | high degree | Transparent | Shangha |
| 2 | trimethoxy silane | C911251NO3 | 221.372 | of purity | without color | i China |
| | (APTMS) | 51 | | of purity | without color | i, Ciina |
| 10 | Ethanol | Сансон | 46.07 | 00.0% | | Sigma |
| 10 | | 02115011 | +0.07 | JJ.J70 | | Aldrich |
| 11 | Centrifuging | | | | | China |
| 12 | Liltrasonic | | | | | China |
| 14 | Onasonie | ······ | | | | Cinna |

| 13 | Oven Jrad | | Steles steal | Syria |
|----|------------------|------|------------------|-------|
| | | | | |
| 14 | Hot furnace up | | Ceramic and | Iraq |
| | 5000 | | stear | |
| 15 | Magnetic stirrer | | Plate of steal | Iraq |

2.2.2.A. Graphene Oxide Preparation

Hummers method was applied to product graphene oxide (GO) [126] 1 g from graphene powder with particle size 6-8 nm was added to 23ml of H_2SO_4 98% with 5g of sodium nitrate NaNO₃ for 15 min.

Then 3g of KMnO₄ 99 % was mixed with deionized water 500 ml and the solution putted on the magnetic stirrer for 24 h at 35C° then diluted with 5 ml, H_2O_2 (30%) was added. The solution was washed by 5%M of HCl (11.25) + H_2O (88.75) 37.5%. Finally, to obtain the solution of GO must heated at 100 C° for 3 h.

2.2.2B. Synthesis ZNR@Gr core-shell Catalysis

Electrostatic self-assembly method was used to cover ZNR arrays with graphene. The ZNR surface can be modified with APTM amino-propyl trimethoxy silane, in 5% ethanol solution /APTMS obtained a positive charge surface and 5 mL 0.1 mg mL⁻¹ negative charge. Go is prepared by using the modified Hummers' methods as shown in fig. (2.2).

Using centrifuging at 8000 RPM for 25 min. Then dilute with 100 mL of water to treat by ultrasonic for 20 min. Converted samples can be submerged in GO solution with heating at 65 C° for 4 h. Deionized water will purify the samples and execute them at 65 C°.

Lastly, to get the ZNR@ GO core-shell should anneal at 500 C $^{\circ}$ for one hour to obtain ZNR@Gr core-shell.



Figure. (2.2). *The ZNR coated stapes with graphene (ZNR@Gr core-shell) a. APTMS/ethanol solution a. appositively charges solution b. graphene oxide (GO) negatively charge solution c. FTO substrate with ZNR@GO core-shell. d. FTO substrate with ZNR@Gr core-shell.*

2.2.3. Synthesis ZNR@Gr/Cu core-shell and ZNR/Cu core-shell Catalysis

To synthesis ZNR@Gr/Cu core-shell and ZNR/Cu core-shell catalysis different material and device have been used materials and device as exhibited in table (2.3).

| No | Chemical - material | Chemical - formula | Molecular Weight (g/mol) | Purity % | Physical form | Purveyor |
|----|--------------------------------|--|--------------------------------|----------|---------------|--|
| 1 | Copper (II) chloride | HCuCl ₄ | 170.48 | 99% | Green powder | Sigma- Aldrich |
| 2 | Kupfer (II)- chloride | CuCl ₂ | 99.00 | 98% | Yellow powder | Sigma- Aldrich |
| 3 | Polyvinyl alcohol (PVA), | C ₄ H ₆ O ₂ C ₂ H ₄ O | 67.00 | 99% | White powder | Sigma- Aldrich |
| 4 | Cu - nanoparticle | Cu NP | | 99% | Brown powder | Nanjing nano technology China |

Table (2.3): The chemical materials and device characteristics applied to form ZNR@Gr /Cu core-shall and ZNR/Cu core-shall.

| 5 | Sodium borohydride | NaBH4 | 37.83 | 98% | white microcrystalline powder | Sigma- Aldrich |
|---|-----------------------|------------------|-------|--|-------------------------------------|-------------------|
| 6 | Oven Jrad | | | | Steles steal | Syria |
| 7 | Magnetic stirrer | | | | Steel plate | China |
| 8 | Deionized Water | H ₂ O | | high degree of purity - empty of additional ions | | Iraq |

0.1mL HCuCl₄ (25mM) mixed with 0.15 mL CuCl₂ (25 mM) solutions of aqueous can be added in a 50 mL beaker with deionized water, 50 m PVA from (PVA/(Cu) 0.5 g, weight ratio), Cu NP size range (10-15) nm and NaBH₄ (NaBH4/(Cu) 5, molar ratio) mingled solution as mixed with stirred continuously into the beaker. The formed ZNR and ZNR@Gr core-shell is submerged in the solution for 4 h and cleaned by deionized water. Then ZNR@Gr/ Cu core-shell and ZNR/Cu core-shell samples were obtained after drying at 70C° for 1 h, as represented in fig. (2.3).



Figure. (2.3). The synthesizes steps of, ZNR@Gr/Cu core-shell and ZNR/Cu core-shell Catalysis.

2.2.4. Preparation of ZNR/Cu Ag core-shell co and ZNR@Gr/Cu Ag core- shell Catalysis

To synthesis ZNR@Gr/Cu Ag core-shell and ZNR/Cu Ag core-shell catalysis have been used materials and device were exhibited in table (2.4).

Table (2.4): The chemical materials and device characteristics applied to form ZNR@Gr /Cu Ag core-shell and ZNR/Cu Ag core-shell.

| No | Chemical - material | Chemical - formula | Molecular Weight (g/mol) | Purity % | Physical form | Purveyor |
|----|---------------------------------|--|--------------------------------|--|-------------------------------------|--|
| 1 | Copper (II) chloride | HCuCl ₄ | 170.48 | 99% | Green powder | Sigma- Aldrich |
| 2 | Silver chloride | AgCl ₂ | 178.77 | 99% | White Solid powder | Sigma- Aldrich |
| 3 | Polyvinyl- alcohol (PVA), | C ₄ H ₆ O ₂ C ₂ H ₄ O | 67.00 | 99% | White powder | Sigma- Aldrich |
| 4 | Sodium borohydride | NaBH4 | 37.83 | 98% | white microcrystalline powder | Sigma- Aldrich |
| 5 | Cu - nanoparticle | Cu NP | | 99% | Brown nano powder | Nanjing nano technology China |
| 6 | Ag - nanoparticle | Ag NP | | 99.9% | Silver nano powder | Oocap France SAS |
| 7 | Oven Jrad | | | | Steles steal | Syria |
| 8 | Magnetic stirrer | | | | Steel plate | China |
| 9 | Deionized Water | H ₂ O | | high degree of purity - empty of additional ions | | Iraq |

 $0.1 \text{ mL HCuCl}_4 (25 \text{ mM})$ mixed with $0.15 \text{ mL AgCl}_2 (25 \text{ mM})$ from solutions of aqueous can be added with deionized water 50 mL in the flask. 50 mL Polyvinyl- alcohol (PVA/ (Cu Ag) (0.5,1) g, weight rate) and NaBH₄ (NaBH₄/ (Cu Ag) NP 5, molar, ratio) mingled sol as stirred into the flask continuously. The formed ZNR/Cu Ag core-shell and ZNR@Gr core-shell then submerged in the sol for 4h thin washed by deionized water. The ZNR/Cu Ag core-shell and ZNR@ Gr/Cu Ag core-shell samples were obtained after drying at 70C° for 1 has represented in fig. (2.4).



Figure. (2.4) Synthesizes the steps of ZNR@Gr/Cu Ag core-shell and ZNR/Cu Ag core-shell catalysis.

2.3. Techniques of Characterization

According on different characteristic of semiconductor photocatalytic materials, many several techniques were used. These properties contain particle size, surface, morphology, crystalline phase, chemical structure, electric and optical characteristic.

The techniques are used for testing the photocatalytic of semiconductor materials implicates Photoluminescence spectroscopy (PL), UVvisible Spectroscopy (UV-VIS), Transmission Electron Microscopy (TEM), Field Emission Scanning Electron Microscopy (FE-SEM), Higher Transmission electron microscopy (HTEM), Zeta Potential analysis.

All these tests used in this work to ensure the photocatalysis with excellent physical properties before used it in photo electrochemical cell to get good enhancement in efficiency of photocatalysis of water splitting.

2.3.1 Structure Measurements

2.3.1.1 Atomic Force Microscopy

The topological properties of the ZNR, ZNR@Gr core-shell, ZNR/Cu core-shell, ZNR/Cu Ag core-shell, ZNR@Gr/Cu Ag core-shell and ZNR/Cu Ag core-shell catalysis can be studied by contact mode of Atomic Force Microscopy (AFM, modal AA 3000 scanning probe microscope from USA and AFM JPK Nano wizard ll Germany). It can be utilized to get the average size of particles and surface roughness of the grown products. (Baghdad University, college of science, chemistry department and Iran).

2.3.2.2 Field Emission Scanning Electron Microscope (FESEM)

The prepared films topography and particle size measurements were studied by busing (FESEM) and Energy dispersive X-ray (EDX) analysis of annealed catalysis were completed by using scanning electron microscopy (SEM; ziess sigma Hv300, Germany and Tescan Mira3 France) The EDX gives quantity and quality for the element's distribution in the sample. (Ministry of Science and Technology and Iran).

2.3.3.3 Transmission Electron Microscopy (TEM)

The prepared topography films measurements were studied Transmission electron microscopy (TEM) Facility (300 kV) @MEMS Germany, Iran) by using analysis of annealed thin films.

2.3.4.4 Higher Transmission Electron Microscopy (HTEM)

Fei-tecnai cryo-bio 200KV FEG-TEM-TEM-TWIN.USA is a 300 kV Transmission Electron Microscope at Company (Advanced laboratory Equipment Department, Iran) by using analysis of thin films as displayed in Fig. (2.10).

2.4. The optical properties Measurements

2.4.1 UV-VIS Spectrophotometer

UV-VIS-NIR 1800 spectrophotometer can be utilized to estimate absorbance and transmittance spectra of nanocomposite thin films in the wavelength range 190 to 1100nm at room temperature. This instrument was computerized with a CRT screen and keyboard for operating the input value. (Baghdad University, college of science, chemistry department).

2.4.2 Photoluminescence spectroscopy (PL)

(RF-530Ipc) instrument (Germany). PL include of a Xenon lamp (Xe) that emits continuum from 300 - 1100 nm using analysis of nanocomposite thin films at Company (Advanced laboratory Equipment Department, Iran).

2.4.3 Zeta Potential analysis

Analysis of Zeta potential (Zeta plus Brookhaven- 90Bundle Instruments Corporation - USA). (Ministry of Science and Technology), it was used to measure the difference of potential between the medium of dispersion and fluid attached stationary layer to the nanoparticle.

2.5 Design and fabrication photo electro chemical cell of photocatalytic setup

All the photocatalytic ZNR, ZNR@Gr core-shell, ZNR/Cu core-shell, ZNR/Cu Ag core-shell, ZNR@Gr/Cu Ag core-shell and ZNR/Cu Ag core-shell were used to experiments for the evaluation of hydrogen. It was achieved into quartz cell with two electrode reference electrode and counter electrode.

The working electrode (all samples or all photo catalysis) was started without light (Dark light) then under laser (410,473,532, and632) nm. The PEC properties were using by an electrochemical workstation E Chem Startup Kits (ER461) from eDAQ compony as shown in fig (2.6).



Figure. (2.6) photoelectrochemical workstation E Chem Startup Kits (ER461) from eDAQ compony.

All thin films can be used as a photoanode or work electrode catalysis and a platinum wire can be applied as a counter electrode, Ag/AgCl saturated electrode

can be applied as a reference as shown in fig. (2.7). The materials and device used are shown in table (2.5).

All tests of the PEC were achieved in Na_2SO_4 solution 0.5 M. The linear sweep voltammograms were tested in the range of 0 - 0.8 V versus Ag/AgCl, and the scanning rate was 10 mV s⁻¹ with 60 s for a cycle.



Figure. (2.7) *photoelectrochemical cell for water spitting setup.*

Table (2.5): Materials and device used in setup of photoelectrochemical cell for water spitting

| No | Material | Chemical - formula | Molecular Weight (g/mol) | Purity% | Physical form | Purveyor |
|----|------------------------|-----------------------|--------------------------------|---------|------------------|-------------------|
| 1 | Reference electrode | Ag/AgCl | | | | eDAQ Australia |
| 2 | a platinum Disk | Pt | | | | eDAQ |

| | | | | | Australia |
|---|----------------|---------------------------------|------|-------|-----------|
| 3 | Quartz cell | | | Glass | eDAQ |
| | | | | | Australia |
| 4 | Sodium sulfite | Na ₂ So ₄ | 99% | | United |
| | | | | | Kingdom |
| 5 | Workstation | ER466 | | | EDAQ |
| | | | | | company |
| | | | | | Australia |
| 6 | Laser | 532 nm | | Green | Diode |
| | | | | light | laser |
| | | | | | China |
| 7 | Laser | 632 nm | | Rad | Diode |
| | | | | light | laser |
| | | | | | China |
| 8 | Laser | 473nm | | Blue | Diode |
| | | | | light | laser |
| | | | | | China |
| 9 | Laser | 410nm | | Blue | Diode |
| | | | | light | laser |
| | | | | | China |

Chapter Three

Results and Discussion

3.1 Introduction

This chapter includes the results and discussions of photocatalyst (working electrode) nanostructured thin films for photo electro chemical cell of water splitting. These results contain the structural results, morphologies properties, optical properties and the results of water splitting illuminated by laser light with different wavelength and power density (410,473,532,632) nm of (100,200, 500, 300) m Wcm⁻².

3.2 Structural Properties Results of Thin Films

3.2-1 Atomic Force Microscopy

The morphological properties of nanostructured ZNR, ZNR@Gr coreshell, ZNR/Cu core shell, ZNR /Cu Ag core-shell, ZNR@Gr/Cu core-shell, ZNR@Gr/Cu Ag core-shell nanocomposite thin films (electrode) prepared by method (chemical reduction method then hydrothermal method) was studied by Atomic force microscopy. All these thin films were coated with graphene by Electrostatic Self-Assembly method, and doped with Cu only and Cu Ag (1:2) nanoparticles powder with average size about (10-15) nm by reduced method. All these thin films deposited on FTO substrates done by atomic force microscopy (AFM) are shown in Fig. (3.1). The calculated values of surface roughness and the average depth are summarized in Table (3.1).

Table (3.1) Calculated values of surface roughness and the average depth of particle size of the thin films.

| Thin films | average depth of | Roughness | |
|-------------------------|---------------------|--------------------|--|
| | particles size (nm) | (Root mean square) | |
| ZNR | 10.05 | 3.5 | |
| ZNR/Cu core-shell | 19.72 | 4.92 | |
| ZNR/Cu Ag core-shell | 30 | 7.12 | |
| ZNR@Gr core-shell | 90 | 22.6 | |
| ZNR@Gr/Cu core-shell | 95.18 | 23.02 | |
| ZNR@Gr/Cu Ag core-shell | 109.77 | 24.1 | |

The table (3.1) and fig. (3.1) show that the morphology of the thin films. All the thin films have a high nature crystallinity. It can be seen that Image (a) is uniform roughness and homogenies of the ZNR, which appeared better nucleation centers for the formation of well arrangement. The average depth less than 10.05 nm with roughness average (3.5nm).



Figure. (3.1) AFM of. (a) ZNR, (b) ZNR/Cu core-shell,



Figure. (3.1). AFM of (c) ZNR/Cu Ag core-shell, (d) ZNR@Gr core-shell

Fig. (3.1) (b) (c), (d), (e) and (f) shows, ZNR/Cu core-shell ZNR/Cu Ag core-shell, ZNR@Gr core-shell, ZNR @Gr/Cu core-shell and ZNR @Gr/Cu Ag core-shell, it could be seen that images are uniform and homogenies, which appeared well arrangement of Cu, Cu Ag nanoparticles powder.

The average depth of ZNR/Cu core-shell is less than 19.72 with roughness (4.92) nm at (b) The average depth of ZNR/Cu Ag core-shell is less than (30)

with roughness (7.12) nm at (c). Image (e), of ZNR@Gr/Cu core-shell with (95.18) nm roughness and the average depth is less than (23.02) nm. Image(f) ZNR@Gr/Cu Ag core-shell with (24.1) nm roughness and the average depth is less than (109.77) nm.



Figure. (3.1) AFM of. (e) ZNR@Gr/Cu core-shell, (f) ZNR@Gr/Cu Ag core-shell.

Image (d) of ZNR@Gr core-shell, was uniform with average depth less than 90 nm with roughness average (22.6) nm the average size disruption of graphene was not large, that which matches very good with ZNR thin film to prepare the ZNR@Gr core-shell structure, which coincides to 5 layers of Gr these results are similar to these in ref. [127]

3.2.2 Energy Dispersive X-ray Analysis (EDX)

The chemical composition and electronic structure of the atoms in the ZNR, ZNR@Gr core-shell, ZNR/Cu core-shell, ZNR /Cu Ag core-shell, ZNR@Gr/Cu core-shell, ZNR@Gr/Cu Ag core-shell nanocomposite thin films(electrode) was investigated by (EDX).

The EDX spectrum shown in fig. (3.2). The EDX Spectrum peaks specified the atom matches to a single component of element in the sample. These figures indicate the electronic transitions from L-shell to K-shell. The EDX spectrum demonstrate that the formed samples are consisting of Zn, Cu, O, Ag, C, and Si from substrate (FTO).

The EDX test discovered the existence of the other elements, defect from the glass substrates (FTO). The atomic percentage was listed in Table (3.2).

| Thin films | element | Atom percentage | Wight percentage | Type electronic transition |
|------------|---------|--------------------|---------------------|----------------------------------|
| ZNR | Zn | 7.58 | 23.22 | L-shell |
| ZNR | 0 | 79.22 | 59.40 | K-shell |
| ZNR | Si | 13.20 | 17.38 | K-shell |

Table (3.2). The weight and atomic percentage of the element's presence in the thin films.

| Total | | 100% | 100% | |
|----------------------|----|-------|-------|---------|
| ZNR@Gr core-shell | Zn | 2.04 | 7.08 | L-shell |
| ZNR@Gr core-shell | 0 | 56.50 | 48.04 | K-shell |
| ZNR@Gr core-shell | С | 19.90 | 12.71 | K-shell |
| ZNR@Gr core-shell | Si | 21.56 | 32.18 | K-shell |
| Total | | 100% | 100% | |
| ZNR/Cu core-shell | Zn | 20.68 | 56.24 | L-shell |
| ZNR/Cu core-shell | 0 | 60.32 | 22.30 | K-shell |
| ZNR/Cu core-shell | Si | 10.18 | 6.24 | K-shell |
| ZNR/Cu core-shell | Cu | 8.82 | 15.22 | L-shell |
| Total | | 100% | 100% | |
| ZNR@Gr/Cu core-shell | Zn | 2.15 | 7.26 | L-shell |
| ZNR@Gr/Cu core-shell | 0 | 45.88 | 37.82 | K-shell |
| ZNR@Gr/Cu core-shell | Si | 19.17 | 27.75 | K-shell |
| ZNR@Gr/Cu core-shell | С | 30.21 | 18.69 | K-shell |
| ZNR@Gr/Cu | Cu | 2.59 | 8.48 | L-shell |
| Total | | 100% | 100% | |
| ZNR/Cu Ag core-shell | 0 | 57.84 | 23.88 | K-shell |
| ZNR/Cu Ag core-shell | Zn | 8.83 | 14.89 | L-shell |
| ZNR/Cu Ag core-shell | Si | 7.07 | 5.12 | K-shell |
| ZNR/Cu Ag core-shell | Cu | 14.85 | 24.36 | L-shell |

| ZNR/Cu Ag core-shell | Ag | 11.41 | 31.75 | L-shell |
|-------------------------|----|-------|-------|---------|
| Total | | 100% | 100% | |
| ZNR@Gr/Cu Ag core-shell | Zn | 3.25 | 5.97 | L-shell |
| ZNR@Gr/Cu Ag core-shell | 0 | 42.42 | 19.09 | K-shell |
| ZNR@Gr/Cu Ag core-shell | Si | 5.57 | 4.40 | K-shell |
| ZNR@Gr/Cu Ag core-shell | С | 20.97 | 7.08 | K-shell |
| ZNR@Gr/Cu Ag core-shell | Cu | 16.72 | 29.88 | L-shell |
| ZNR@Gr/Cu Ag core-shell | Ag | 11.07 | 33.59 | L-shell |

The (EDX) given in the fig. (3.2) (a) shows the presence of (Zn, O) and Si, comes from the substrate, that means the formation of the crystallinity structure was due to the presence of a suitable surfactant. A good reacting intensity with Zn, Cu, Ag and C have been observed at fig. (a, b, c, d, e, f).

Fig. (3.2). (b) refers to Zn, O, C and Si from substrate graphene appeared and intensity of (O) increased when coated the ZNR by graphene, (c) refers to (Zn & Cu) with high intensity beak was good reacting when doped the ZNR, by Cu ((10-15) nm NP powder) and without Gr coated.

Then at (d) the intensity of C, with the seam intensity at (b)that means good reacting between Zn & Cu but the intensity of Cu larger than Zn while at (c) the intensity of Zn was larger than Cu NP according to the electronic transition from L-shell to K-shell.


Figure. (3.2). (EDX) for a. ZNR, b. ZNR@Gr core-shell, c. ZNR/Cu core-shell d. ZNR@Gr/Cu core-shell, e. ZNR/Cu Ag core-shell and f. ZNR@Gr/Cu Ag core-shell electrode.

3.2.3 Field Emission Scanning Electron Microscope (FESEM)

The morphological changes of the prepared ZNR, ZNR@Gr core-shell, ZNR/Cu core-shell, ZNR /Cu Ag core-shell, ZNR@Gr/Cu core-shell, ZNR@Gr/Cu Ag core-shell nanostructure. Thin films (electrode) were tested by used Field Emission Scanning Electron Microscopy FESEM can describe the shape and size of samples. Fig. (3.3), (a, b) refers to (ZNR) that grow larger length, high density rod to rod separation and a random arrangement or horizontally growth these results are similar to these in ref. [128].



Figure. (3.3) SEM images (a, b) of ZNR

Fig. (3.3), (c, d) one can observe the wrinkles on the ZNR surface when graphene connecting the ZNR arrays to obtain ZNR@Gr core-shell. That mean the graphene was good coated on the uniformly ZNR thin film, which was not more than 5 layers thick, these results are similar to these in ref. [124]



Figure. (3.3) SEM images of (c, d) ZNR@Gr core-shell

Fig. (3.3), (e, f) are the SEM of ZNR/Cu core-shell, that show the good sprinkled Cu NP on ZNR, with the size of around (10-15) nm, which displays Cu NP random nanoparticle, these results agree with ref. [127]



Figure. (3.3) SEM images (e, f) of ZNR@Gr/Cu core-shell

Fig. (3.3) (g, h) refers the SEM image of ZNR@Gr/Cu core-shell graphene coated generality of the ZNR surface, and Cu NP are equal distributed

on the surface of ZNR@Gr core-shell. Farther more the Cu NP were shown to be garnished onto the graphene intercourse on the ZNR surface.



Figure (3.3) SEM image. (g, h) of ZNR@Gr/Cu core -shell

In fig. (3.3). (i) of SEM analysis for ZNR/Cu Ag core-shell, which exhibits the well-dispersed Cu Ag NP on ZNR with the size of (10-15) nm, which displays Cu Ag random nanoparticle. SEM image of ZNR@Gr/Cu Ag core -shell

at image (j) graphene-coated the ZNR surface, and Cu Ag NP were uniformly sprinkled on the ZNR@Gr core- shell surface. This result is similar with ref. [129]. The Cu Ag NP can be found to be graced onto the graphic jointed the ZNR of display in the forming structure of ZNR@Gr/Cu Ag core-shell, these results agree with ref. [127]



Figure. (3.3) SEM images (i,) of ZNR/Cu Ag core-shell and SEM image (j) of ZNR@Gr/Cu Ag core-shell

3.2.4 Transmission electron microscopy (TEM)

The morphological of the prepared, ZNR@Gr core-shell, ZNR/Cu coreshell, ZNR /Cu Ag core-shell, ZNR@Gr/Cu ag coreshell nanostructure thin films were analyzed using Transmission electron microscopy (TEM). Fig. (3.4), (a, b,) represented to ZNR@Gr core-shell It was specified from the image in low enlargement that the zinc oxide nanorods are randomly distributed on ZNR@Gr core-shell. The ZnO nanorods were noted very visibly from the high magnification images. It was shown at the TEM picture that the ZNR superficies was good coated by graphene, but it is not more than 5 layers at (a, b). These results are similar to these in ref. [127]



Figure. (3.4) TEM images (a, b) of ZNR@Gr core-shell



Figure. (3.4) TEM images (c) of ZNR/Cu core-shell, (d) of ZNR@Gr/Cu core-shell(e)of ZNR/Cu Ag core-shell

TEM of ZNR/Cu core-shell, ZNR/Cu Ag core-shell, ZNR@Gr/Cu coreshell, ZNR@Gr/Ag Cu core-shell, that exhibited the good sprinkled Cu NP and Cu Ag nano particle powder on ZNR with the average size of around (10-15) nm, which displays Cu NP, Cu Ag NP random core-shell nanoparticle at (c, d, e, f) and provide evidence that powder nanoparticles are directly attached to the ZnO nanorod surface. These results agree with ref. [127,129,130]



Figure. (3.4) TEM images(f) of ZNR@Gr/Cu Ag core-shell.

3.2.5 Higher Transmission Electron Microscopy (HTEM)

The morphological of the prepared, ZNR@Gr core-shell nanostructure thin film (electrodes) was analyzed using Higher Transmission electron microscopy (HTEM). It can be shown in the HTEM picture of the ZNR surface was good coated by graphene uniformly, that was not more than 5 layers at fig. (3.5) (a, b,) These results agree with ref. [127] [131]



Figure. (3.5) HTEM images (a, b) of ZNR@Gr core-shell.

3.3 The Optical Properties Measurements

The optical properties of nanostructured ZNR, ZNR@Gr core-shell, ZNR/Cu core-shell, ZNR/Cu core-shell, ZNR@Gr/Cu core-shell, ZNR@Gr/Cu Ag core-shell nanocomposite thin films deposited on FTO glass substrate (electrodes) were investigated. This involves the absorption, the optical band gab energy E.g., PL spectra, and Zeta Potential analysis.

3.3.1 UV-VIS Spectrophotometer

The UV–VIS absorption spectra of ZNR, ZNR@Gr core-shell, ZNR/Cu core-shell, ZNR /Cu Ag core-shell, ZNR@Gr/Cu core-shell, ZNR@Gr/Cu Ag core-shell nanocomposite thin films are revealed in Fig. (3.6).

All samples, with a high absorption in the ultraviolet region and growth in the light intensity of absorption increased in the range about of 300–1000 nm when coated ZNR by graphene then shifting occurred from UV to Visible region of spectrum. This result is similar with ref. [127]



Figure. (3.6) UV-visible spectra of all thin films.

These raising were exhibited at and ZNR@Gr/Cu Ag core-shell which could be enhanced effect of thin film absorption. This result is similar with ref [127]. The absorption increased when the roughness of the thin films increased as shown at table (1.3).

Fig. (3.7) exhibit that for the optical band gaps of the thin film were obtained when $(\alpha he)^2$ is plotted against photon energy (hv) straight line, which mention that the absorption edge is lead to a direct transition between valence and conduction bands. The intercept of the straight line on the axis matches to the optical band gap (E.g.).

The band gap was degreased at the ZNR 3.2 eV and 2.7 eV of ZNR@Gr core-shell, ZNR/Cu core -shell 2.9 e V, 2.2 eV at ZNR@Gr/Cu core -shell ,2.8 eV ZNR/Cu Ag core-shell and 1.2 eV ZNR@Gr/Cu Ag core-shell, that it causes to a rise in the absorption intensity as double from ZNR to ZNR@Gr/Cu Ag core -shell when refers in that table (3.3) and fig. (3.7).

The energy band gap decreases as the particle size of the semiconductor nanomaterials increased; this result is similar with ref. [130]

| No | Thin films | (E.g) eV |
|----|-----------------------------|----------|
| 1 | ZNR | 3.2 |
| 2 | ZNR/Cu core-shell | 2.9 |
| 3 | ZNR/Cu Ag core -shell | 2.8 |
| 4 | ZNR@Gr core-shell | 2.7 |
| 5 | ZNR@Gr/Cu core-shell | 2.2 |
| 6 | ZNR@Gr/Cu Ag core- shell | 1.2 |

Table (3.3) shows to the values of band energy gap of the thin films



Figure. (3.7) *direct optical energy plotted for all thin films.*

3.3.2 Photoluminescence spectroscopy (PL)

PL spectra of ZNR, ZNR@Gr core-shell, ZNR/Cu core-shell, ZNR /Cu Ag core-shell, ZNR@Gr/Cu core-shell, and ZNR@Gr/Cu Ag core-shell catalysis are revealed in Fig. (3.8).



Figure. (3.8) PL spectra of all thin films.

The recombination of photo excited electron-hole pairs is tested by PL spectra. An emission peak can be noted (300 -600) nm, which is referred to as the emission of band edge generating from the recombination of excitonic centers. [132]

The peak intensity has been reduced after adding Cu Ag or graphene, which be inverted a reduction in the recombination of photo electron-hole pairs of semiconductors. Graphene or Cu, Cu Ag NP obtained excited electrons in the CB to split up the electron-hole pairs and the energy gap of ZNR was reduced when combining with Cu, Cu Ag or graphene because SPR effect occur. [133]

ZNR@Gr/Cu Ag core-shell displayed the weakest UV emission. The exposed surface can be garnished with Cu, Cu Ag NP, which was more reduced the recombination of photo electron hole pairs. ZNR displayed intensive emission at VIS light regain, however the intensity of emission decreases after incorporating with graphene, Cu and Cu Ag because SPR effect occur. The results, agree with.[134]

3.3.3 Zeta Potential analysis

The surface charge of the Cu and Cu Ag nanoparticles diluted by the solvent solution used to immerse the thin films or electrode ZNR and ZNR@Gr core-shell to obtained the ZNR/Cu core-shell, ZNR/Cu Ag core-shell, ZNR@Gr/Cu core -shell and ZNR@Gr/Cu Ag core-shell was measured by zeta-potential. In general, the stability of a surface against agglomeration was measured by zeta -potential.

Increasing in zeta potential value suggest that the stability of Cu and Cu Ag nanoparticles solution reluctance of nanoparticles to collection and obtained power electric disaccord between them. That indicates high stability of these nanoparticles. The value of the particle surface charge is important to understand the behavior between the particles in the solvent and indicate the stability of ZNR/Cu core-shell, ZNR/Cu Ag core-shell, ZNR@Gr/Cu core-shell and ZNR@Gr/Cu Ag core shell nanoparticles thin films, where the increased for zeta potential of colloids (negative or positive) lead to increase the electrical stability, while reduced value of zeta potentials refers to aggregate and agglomerate. Nanoparticles with Zeta potential value more than +30 mV or less than -30 mV are typically.[135]

Zeta potential surface charge for Cu and Cu Ag nanoparticles solution was illustrated in Fig. (3.9), and (3.10), it has a very good stability, the observed zeta potential values and mobility values for the samples are illustrated in the table (3.4) as follows:

Table (3.4): The values of the zeta potential and the mobility of Cu and Cu Ag nanoparticle solution.

| The nano particle solution | Zeta potential (mV) | The mobility (m ² V ⁻¹ s ⁻¹) |
|----------------------------|---------------------|--|
| Cu | - 19.81 | - 1.55 |
| Cu Ag | - 15.92 | - 1.24 |





(b)

Figure. (3.9). (a) The zeta potential (mv) of Cu nano particle solution; (b) the mobility ($m^2 V^{-1} s^{-1}$) of Cu nano particle solution.





(b)

Figure. (3.10). (a) The zeta potential (mv) of Cu Ag nano particle solution; (b) the mobility (m2 V-1 s-1) of Cu Ag nano particle solution.

3.4Characterization of photoelectrochemical performances

3.4.1 The experimental performances at dark current density

The photoelectrochemical cell representation was measured with electrochemical Workstation from (ER466, EDAQ company Australia, potential stat) by three-electrode.

To study the behavior of graphene and Cu, Cu Ag nanoparticles First, the samples of ZNR, ZNR/Cu core-shell, ZNR@Gr/Cu core-shell, ZNR/Cu Ag core-shell, ZNR@Gr core-shell, and ZNR@Gr/Cu Ag core-shell were tested in the Dark current density as shows in fig. (3-11).



Figure. (3.11). (a) *Experimental at Dark current density(b) All samples used as working electrode (c)Counter electrode Pt and reference electrode Ag/AgCl.*

The result of all samples is a given at table (3.7) and fig. (3.12). The current density of the electrode increased significantly, at given voltage (0 - 0.8) v versus Ag/AgCl 60 s for a cycle.

| NO | The samples | J Dark mAcm ⁻² |
|----|-------------------------|---------------------------|
| 1 | ZNR | 7.031* 10 -5 |
| 2 | ZNR/Cu core-shell | 1.03* 10 -4 |
| 3 | ZNR/Cu Ag core-shell | 1.01*10 ⁻³ |
| 4 | ZNR@Gr core-shell | 5.2*10 ⁻³ |
| 5 | ZNR@Gr/Cu core-shell | 1.01* 10 ⁻² |
| 6 | ZNR@Gr/Cu Ag core-shell | 1.2*10 ⁻² |

Table (3.5): The values of the J_{Dark} of the all samples at 0.8 v.



Figure. (3.12) Dark current density of (ZNR, ZNR/Cu core-shell, ZNR/Cu Ag core-shell, ZNR@Gr core-shell, ZNR@Gr/Cu core-shell, ZNR@Gr/Cu Ag core-shell) working electrode.

As shown in table (3.6) and fig. (3.12) the current density of ZNR working electrode increased from (7.031* 10⁻⁵ to 1.03*10⁻⁴) mAcm⁻² when added Cu nanoparticles at ZNR/Cu core-shell working electrode, and it is reached to (1.01* 10⁻³) mA cm⁻² when the ZNR decorated by Cu Ag nanoparticles at ZNR/Cu Ag catalysis. The Cu and Cu Ag metal nanoparticles are useful for the electrons transfer from the metal nanoparticle to ZNR also it has good behavior on improving the electrode conductivity. [137]

The current density of ZNR working electrode increased from (7.031* 10⁻⁵ to 5.2* 10⁻³) mA cm⁻² when coated by graphene at ZNR@Gr core-shell working electrode and it is reached to (1.01*10⁻²) mAcm⁻² when it is added Cu nanoparticles at ZNR@Gr/Cu core-shell sample (working electrode). In general graphene is a 2D material with good electrical conductivity and Cu Ag nanoparticles has excellent behavior on improving the electrode conductivity.

The super enhancement of conductivity occurs at ZNR@Gr/Cu Ag coreshell working electrode the current density is reached to $(1.2*10^{-2})$ mAcm⁻² when the ZNR working electrode is coated and decorated by Cu Ag because the ZNR is used the advantage of two previous features at the same time. [138]

3.4.2 The experimental performances under illuminated of (410, 473, 532 and 632) nm laser light

The catalysis photocurrent densities for ZNR, ZNR/Cu core-shell, ZNR/Cu Ag core-shell, ZNR@Gr core-shell, and ZNR@Gr/Cu Ag core-shell were tested under laser irradiation with different wave length (410,473,532,632) nm of (100,200, 500, 300) m Wcm⁻², at 0 - 0.8 V versus Ag/AgCl ,60 s for a cycle.as shown in Fig. (3.13)(a, b, c, d).





Figure. (3.13). *Experimental at illumined by laser light (a) (437) nm, (b) (532) nm (c) (632) nm, (d) (410) nm*

The result in table (3.6) and fig (3.14) (a) for ZNR working electrode the current density increased when illuminated by laser light 410 nm from (0.931to 2.892) m A cm^{-2,} when added Cu nanoparticles at ZNR/Cu core-shell working electrode, then increased to (2.929) mAcm⁻²

| NO | The samples | J laser (410nm) mA cm ⁻² at (100 mw cm ⁻²) | J laser (473nm) mA cm ⁻² at (200 mw cm ⁻²) | J laser (532nm) mA cm ⁻² at (500mw cm ⁻²) | J laser (632nm) mA cm ⁻² at (300mwcn ⁻²) |
|----|-----------------------------|---|---|--|---|
| 1 | ZNR | 0.931 | 0.622 | 0.782 | 0.362 |
| 2 | ZNR/Cu core-shell | 2.892 | 1.847 | 1.988 | 1.801 |
| 3 | ZNR/Cu Ag core-shell | 2.929 | 2.034 | 2.135 | 2.001 |
| 4 | ZNR@Gr core-shell | 4.213 | 2.622 | 2.593 | 2.432 |
| 5 | ZNR@Gr/Cu core-shell | 4.622 | 3.327 | 3.451 | 2.899 |
| 6 | ZNR@Gr/Cu Ag core- shell | 5.210 | 3.662 | 3.927 | 3.112 |

Table (3.6): The values of the J laser (410,473,532,632nm) of the all samples.

at ZNR/Cu Ag core-shell, metal nanoparticles are useful for the electrons transfer from the metal nanoparticle to ZNR sample also it has good behavior on improving the electrode conductivity. [137] It is well-known that when the size of nanometer-scale metal is lower than the light of incident lead to create hot electrons can be increased absorbed of material, which is named surface plasmon resonance (SPR). [139]

In addition, the photo current density of ZNR@Gr core-shell raised to (4.213) mA cm⁻² at 0 - 0.8 V versus Ag/AgCl ,60 s for a cycle., compared with current density of ZNR was (0.931) mA cm⁻² after coating with graphene under illuminated by laser light 410 nm. Moreover, the current density reached to (4.622) mAcm⁻² at ZNR@Gr/Cu core-shell working electrode.

When the two metal Ag and Cu nanoparticles are combined with ZNR@Gr core-shell sample, the current density of ZNR@Gr/Cu Agcore-shell sample

increased three orders of magnitude compared with the current density of ZNR which was that of ZNR under the seam laser light 410 nm because the ZNR is used the advantage of three previous features at the same time.

First the effected of nanoparticle, the second effected of the graphene, it has a resonant at IR regain and third is the effect of SPR to improve the efficiency of ZNR working electrode. [138 -139]





Figure. (3.14) current density under laser illuminated of All catalyzes (a) All samples illuminated by 410 nm laser light, (b) All samples illuminated by 473 nm laser light, (c) All samples illuminated by 632 nm laser light and(d) All samples illuminated by 532 nm laser light.

The result in table (3.7) and fig (3.14) (b)and (c) for ZNR, compared to the photocurrent densities of, ZNR/Cu core-shell, ZNR/Cu Ag core-shell, ZNR@Gr core-shell, ZNR@Gr/Cu core-shell and ZNR@Gr/Cu Ag core-shell catalyzes increased when illuminated by laser light 473nm and 632 nm, the results

appeared approximately is the seam increasing at the current density of all samples because the is nearly similar and this result matched with the UV-visible test in figure (3.6) at page 57.

Moreover, the result of illuminated the all samples by 532nm laser light display the same behaver with 473 and 632nm but with same increased with current density at all the samples that accrued because the power of 532 nm laser light was 500 m W cm⁻² compared with 200,300 m W cm⁻² for 473 nm and 632 nm. The increasing of power forced the current density of all samples increased at 532nm.

In general, the results indicate that ZNR electrode covering with graphene or decorated with Cu only or, Cu Ag nanoparticles or, coating and decorated with Cu only or, a Cu Ag nanoparticle can excellently improve the PEC efficiency of the ZNR electrode.

3.5. The efficiency of catalysis

The hydrogen production efficiency (η) for ZNR, ZNR/Cu core-shell, ZNR/Cu Ag core-shell, ZNR@Gr core-shell, ZNR@Gr/Cu core-shell and ZNR@Gr/Cu Ag core-shell electrodes at illuminated different laser wavelength and different power density (410, 473, 532 and 632) nm (100, 200, 300 and,500) m W cm⁻² at (0 - 0.8) V versus Ag/AgCl nm were studied by employ the next equation: [140]

 $\eta = [I (1.23 - E \text{ bias})/J_{light}] \times 100\%$ -----(3-1)

When, (I) refers to the photocurrent density (mA cm⁻²), E bias is the used potential, 1.23 is the criterion of potential of water splitting, and J $_{light}$ refers to the incident intensity of laser. The result as shown in fig. (1-15).





Figure. (3.15) The calculated efficiency of ZNR, ZNR/Cu core-shell, ZNR/Cu Ag core-shell, ZNR@Gr core-shell, ZNR@Gr/Cu core-shell and ZNR@Gr/Cu Ag core-sell as defined in eqn (1-3). (a)the efficiency of all samples under 410 nm illuminated (b) the efficiency of all samples under 473 nm illuminated (c)) the efficiency of all samples under 523 nm illuminated (d)) the efficiency of all samples under 632 nm illuminated.

The result suggested that highest efficiencies with illumined by laser 410 nm ,100 mWcm⁻² was 0.40% ,1.24%1.26%,1.81% ,1.98% and 2.24 % for ZNR, ZNR/Cu core -shell, ZNR/Cu Ag core- shell, ZNR@Gr core-shell, and ZNR@Gr/Cu Ag core-shell samples respectively, compared with another wavelength.

Farther more, the huge efficiency for ZNR@Gr/Cu Ag core-shell sample refers to further improve in the efficiency of hydrogen production. therefore, ZNR@Gr/Cu Ag core-shell as the electrode of PEC is the Super favorable material for water splitting as shown in fig (3.15) (a). Because of the effected of SPR lead to huge super absorption occurs at that sample 2.24%.

Farther more, the result of illuminated from table (3.8) and figure (3.16) (b), (d) the all samples by (473 and 632) nm laser light at 200,300) mWcm⁻² have

approximately the near behaver of the value of efficiency but not the same value, it has the near response of light absorption but different in intensity of light was used this result is matched with the UV-visible test in figure (3.6) at page 57.

Moreover, the efficiency increased at UV and Visible region of light spectrum of all electrodes, but excellent enhancement of efficiency occurs at UV region compared with visible region of light because the current density and absorption value of light for all electrode at that region is more than visible region of light.

It is known the ZNR electrode has a good absorption at UV region of spectrum compared with Visible region of light but when it coated by graphene and doped by Cu and Cu Ag nanoparticle the absorption at visible region increased spatially at sample ZNR@Gr/Cu Ag core -shell.

On the other hand, the intensity of the incident light is inversely proportional with the efficiency according the eq (3-1), therefore the efficiency reduced for (532 nm,500 m W cm⁻²) at all samples compared with other wavelength as shown in table (3.8) and figure (1.15) (c).

In general, all samples electrode or (photocatalysis) have a good increased in efficiency at different wavelength and intensity of light. But the super improving effect occurs at laser 410 nm ,100 m W cm⁻²) spatially at samples ZNR@Gr/Cu core-shell and ZNR@Gr/Cu Ag core- shell.

It has increased in absorption at that wave length and good reduced in energy gap, high reduced in recombination of photoelectron- hole pairs, and good increased of current density and effected of SPR. All that properties can excellently improve the PEC efficiency of the ZNR electrode. This result agrees with ref. [127]

3.6 The Stability of catalysis

To estimate the stability of the ZNR, ZNR/Cu core-sell, ZNR/Cu Ag coreshell, ZNR@Gr core-shell, ZNR@Gr/Cu core-shell and ZNR@Gr/Cu Ag coreshell photoelectrodes in light cycles 60 s and for 480 s were tested at 0 - 0.8 V versus Ag/AgCl at the higher intensity illuminated 500 m Wcm⁻²as shown figure (3.16). The result suggests the current density of working electrode increased under laser irradiation with wavelength (532) nm of (500) m Wcm⁻².



Figure. (3.16) shows the stability of ZNR, ZNR/Cu core-shell, ZNR/Cu Ag core-shell, ZNR@Gr core-shell, ZNR@Gr/Cu core-shell and ZNR@Gr/Cu Ag core-shell samples under laser light 532 nm illuminated.

The stability of ZNR sample reduced after 480 s from 0.782 to 0.310. The different between the two value is (0.472), when subtracting this result from 1% the value of stability. The result found the stability of ZNR is 53%, and by the

same way the stability of onther samples (ZNR/Cu core-shell, ZNR/Cu Ag core-shell, ZNR@Gr core-shell, ZNR@Gr/Cu core-shell and ZNR@Gr/Cu Ag core-shell) are (61.5% ,77%,79%,81%, and 95%).

In general, it could find that the photocurrent at 480 s declining for all samples, due to the photo corrosion of ZnO. That decayed is reduced when ZNR decorated by Cu, Cu Ag and at samples ZNR/Cu core-shell and ZNR/Cu Ag core -shell and stability increased as display at fig (3.16).

In addition, results display that the mixture of Cu, Cu Ag nanoparticles and graphene is excellent for improving the stability and reduced corrosion, the stability of ZNR@Gr/Cu Ag electrode reached to 95 %, therefor it huge available to get of H_2 . This result is similar with ref [127].

3.7 Conclusions

1- All working electrode (photocatalysis) have a good increased in efficiency at different wave length and intensity of light. But the super improving effect occurs at laser 410 nm ,100 m W cm⁻²).

2 - Under the comprehensive effect of Cu, Cu Ag nanoparticles and graphene, the photoelectrochemical cell efficiency and stability exhibited huge enhancement, and this samples (photo electrode) or catalysis (ZNR@Gr/Cu coreshell and ZNR@Gr /Cu Ag core-shell) are suitable for application in H₂ generation.

3.8 Future work

- **1-** Using two metal oxide semiconductor such as ZnO/WO₃ to synthesis ZnO/WO₃@Gr/Ag Cu thin films to enhanced the efficiency of the photocatalysis of water splitting.
- **2-** Using three types of nanoparticles such as (Ag-Cu-Al) in the same range of nm to improve the physical properties of the catalysis.
- **3-** Applied other application with water splitting such as Water pollution.
- 4- Studying laser-induced photocatalysis with increasing the exposure times and temperature.

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الخلاصي

مع زيادة الحاجة العالمية لإيجاد بدائل للطاقة النظيفة والصديقة للبيئة ، أصبحت الخليه الكهروضوئية(PEC) لتقسيم الماء إلى وقود هيدروجيني قابل للتخزين عن طريق الاستخدام المباشر للطاقة الضوئية تقنية جذابة للغاية الآن.

يتكون هذا البحث من خطوات رئيسية لدراسة أشباه الموصلات الضوئية. الخطوة الأولى هي تصنيع أكسيد الزنك النانوي (ZNR) باستخدام طريقة الاختزال الكيميائي والطريقة الحرارية المائية. الخطوة الثانية هي أكسيد الجرافين المُصنَّع (GO) بطريقة همر لتغطية ZNR بطريقة التجميع الذاتي الكهروستاتيكي لتشكيل ZNR (GO core- shell بطريقة مع توزيع النحاس النانوي على ZNR و Gr core- shell ، وكذلك توزيع النحاس والقضه النانوي على ZNR و على ZNR و Gr core- shell ، وكذلك توزيع النحاس والقضه النانوي على RNR و بأطوال موجية مختلفة وطاقات مختلفة (410 ، 704 ، 532 ، و 63) نانومتر ، (100 ، 200 ، 500 ، 300 روس 300) ملي واط / سم²⁻.

تم استخدام خلية كهر وكيميائية ضوئية ثلاثيه القطب ، قطب مرجعي AgCl / AgCl ، قطب جامعPt سلك وقطب كهربائي محفز (catalysis). أُضيئت كل هذه العينات بواسطة ضوء الليزر بأطوال موجية مختلفة (catalysis) ، و 200،000 ، و 300)ملي واط سم²⁻ مختلفة (100،200،500 ، و 300)ملي واط سم²⁻ تم فحص الأشكال والخصائص البصرية لجميع العينات من خلال تقنيات مختلفة مثل المجهر الإلكتروني تم فحص الأشكال والخصائص البصرية لجميع العينات من خلال تقنيات مختلفة مثل المجهر الإلكتروني الإلكتروني عالي وفوق البنعاث الميداني (PESEM) ، المجهر الإلكتروني للإرسال (TEM) ، المجهر الإلكتروني عالي المسح الانبعاث الميداني (PESEM) ، المجهر الإلكتروني للإرسال (TEM) ، المجهر الإلكتروني الورسال (AgC) ، مقياس الطيف الضوئي بالأشعة المرئية وفوق البنفسجية ، مطيافية التألق (PL) ، وإمكانات زيتا.

تُظهر المركبات النانوية ZNR @ Gr / Cu Ag core- shell سلوك امتصاص عالي في منطقة الأشعة فوق البنفسجية (UV) من الطيف. بالمقارنة مع ZNR ، حيث اظهرت العينة / UV @ Gr @ Gr الأشعة فوق Cu Ag core- shell عن امتصاص فائق في المدى 387-1000 نانومتر. واظهرت النتائج نقصان فجوة الطاقه إلى 1.2 فولت ZNR @ Gr / Cu Ag core- shell. شحنة زيتا السطحية المحتملة لحل الجسيمات النانوية Lu و Gu Ag core- shell استقرار في البيانات. استخدم هذا العمل جميع العينات في تطبيق تقسيم الماء باستخدام محطة عمل كهر وكيميائية (EChem Startup Kits (ER461) من مجموعة QAQ من مجموعة QAQ الماء باستخدام

وكانت النتائج ،أولاً كانت جميع العينات التي تم قياسها بكثافة تيار الظلام عند 0 - 0.8 فولت مقابل Ag/AgCl معدل مسح 10 مللي فولت في الثانية مع 60 -s ثانية للدورة. أشارت النتيجة إلى أن التحسين

وزارة التعليم العالي والبحث العلمي جــامعه بــغداد



تحسين المحفز الضوئى لفصل الماء بالرنين البلازمي بأضاءة الليزر

اطروحه مقدمه الى معهد الليزر للدراسات العليا / جامعه بغداد / لاستكمال متطلبات نيل شهاده دكتوراه فلسفه في فيزياء /الليزر

