

## Summery

In the present century, there is quite an extensive diversity of hazards involved with growing energy consumption along with increasing population and improving industrialization. There are potential risks with regard to carbon footprint, greenhouse gases and global warming; the underlying fact is that fossil fuels not only have irreparable damages to the environment but also its shortage must be considered as the main objection. The consequential way to tackle this problem is conventional fossil fuels alternate with bio-friendly energy resources. Having increased society's demand, the research is focused on design and organization power sources devices. To fulfill such targets, the main aspect of efforts is producing energy in a greener pathway. Hydrogen produced from water is one of the renewable energy forms that embraces this target. Suzuki–Miyaura and Stille coupling reactions are one of the main innovative pathways for the synthesis of biphenyls as versatile organic intermediates. Over the past few decades, Pd-catalyzed C–N and C–C coupling reactions have become widespread because of their good selectivity, fast reaction rates, high production yield, and high turnover frequency in various synthetic protocols. However, Pd-based catalysts are expensive, sensitive to air and moisture, get easily poisoned, and require the addition of an organic ligand which pollutes the environment and causes product separation issues. Use of heterogeneous catalysts can possibly be the way forward to solve this problem. Additionally, it must be mentioned that environmental contamination comprises water-, soil-, and air pollution that has been commonly caused by using poisonous/hazardous chemicals, namely, nitrophenols, heavy metals, and organic dyes, among others. Two main types of pollutants such as nitro compounds and toxic dyes are mostly used in diverse industries, e.g., drugs, papers, ceramics, cosmetic printing, food processing, and especially textiles. The toxic nitrophenols (especially 4-NP) are largely responsible as

the main environmental pollutants and must be converted into harmless aminophenols (especially 4-AP) that are prospective intermediates and precursors for pharmaceuticals, synthetic resins, pesticides, and dyes ideally via a reductive protocol. Another hazardous heavy metal in wastewater is [Cr(VI)], produced during some large-scale industrial processes. Trivalent chromium [Cr(III)], in contrast, has 100-fold less toxicity and can be efficiently eliminated via the formation of insoluble hydroxides in water under controlled conditions. Consequently, it is obligatory to develop efficient, ecofriendly, and sustainable methods for the treatment of nitro compounds, organic dyes, and heavy metals, thus addressing both the energy demand and environmental issues; the assembly of nanocomposites and modified nanoparticles does inspire newer strategies for the degradation of pollutants and environmental remediation.

In this thesis, a fast and cost-effectiveness method was deployed to synthesis Palladium nanoparticles (Pd NPs). The Pd NPs were immobilized on the surface of different substrates and used in environmental remediation and hydrogen storage, which are the most pioneering fields in the last and present decades. This thesis was separated to four parts, which try to represent a suggestion to deal with the aforementioned concerns.

In the first part, Pd NPs was produced by Laser ablation in liquid (LAL) and chemical reduction methods and was deposited on the surface of kaldness biomedica filter (KBM). The KBM was purchased from Tianda chemical Industrial (PE03, density =  $155 \text{ kg m}^{-3}$ , specific surface area  $> 834 \text{ m}^2/\text{g}$ , material = High density polyethylene (HDPE)). The morphology, structure and composition of Pd/KB nanocomposite were characterized by SEM, TEM, XRD, EDX and UV-Vis spectroscopy.

The LAL process was performed by Fiber laser in deionized water. The Palladium target was immersed in deionized water in a way that 2 mm of water covered the surface of target and laser beam was focused on the surface. During laser irradiation the color of water turn to dark brown, which is an evidence for attendance of Pd NPs. The UV-vis analysis was conducted to detect Pd NPs in deionized water, and the absorption peak around 250 nm shows Pd NPs was successfully fabricated. Unfortunately Pd NPs produced by LAL could not loaded on the surface of KBM, which was confirmed by Scanning electron microscopy (SEM). To produce Pd NPs, the chemical reduction method was deployed and the UV-vis spectrum suggested chemical reduction was managed to produce Pd NPs. The Pd NPs was deposited by physical mixing (stirring 24h, room temperature) and dried in oven, which was named KBM/Pd-ch. Changing color of KBM after deposition recommended the adapted method was succeeded. Different techniques namely X-ray diffraction (XRD), Transmittance electron microscopy (TEM), energy-dispersive X-ray spectrometry (EDX), and Thermogravimetric analysis (TGA) were utilized to characterize synthesized nanocatalyst. The XRD pattern was used to elucidate the structures of samples. Throughout XRD patterns of KBM and KBM/Pd-ch, it can be seen that the characteristic diffraction peak of these samples exhibits a strong peak at  $21.6^\circ$ , also a less intensive peak at  $24.0^\circ$  due to the typical orthorhombic unit cell structure of (110) and (200) reflection planes from HDPE (JCPDS 53-1859), respectively. On top of that the XRD pattern of S2 shows a reflection peak at  $49.119^\circ$  derived from the ordered arrangement of (111) plane of the Pd (JCPDS 46-1043). This peak shows that Pd NPs were decorated on HDPE in dominate (111) plane. Using Bragg's law and data of XRD, the lattice constant of Pd NPs was estimated about  $3.89 \text{ \AA}$ , which is in a good agreement with other reports. Morphology of samples was studied by using SEM equipped with

EDX detector. SEM images of fracture surface of KBM and KBM/Pd-ch with different magnification. The images of SEM clearly shows a typical ocean-like, porosity surface and lamellar structure of the KBM. This porosity provides a good space for deposition. According to SEM images, the Pd NPs wasn't uniformly deposited on the surface of the samples. Also, the comparison of SEM images clearly shows that the surface became slightly smoother for influence of Pd NPs on the surface. The elemental composition of samples was studied by EDX analysis. Comparison of EDX analysis of samples revealed that Pd NPs are deposited on the surface of samples which is agreed with XRD and SEM analyses. The EDX mapping analysis demonstrated the Pd NPs were random distributed on KBM surface. The functional groups of samples was studied by FTIR spectra and the results suggest that the main groups of HDPE was detected. Comparison of spectrum shows that after Pd NPs deposition the spectra did not alter because Pd NPs was physically loaded. To assess the thermal stability of polymeric nanocomposites, TGA analysis was used. The TGA curve was drawn by the massloss behavior as a function of temperature. Through the curves both samples display similar thermograms with a single massloss zone centered around 180 °C. The Pd NPs affect the thermal stability of the pure samples negatively as the curves shown. We have to consider that deposition of Pd NPs on pure samples shifts the TGA curves to lower temperatures but it isn't significantly which is probably related to the thermal conductivity of Pd NPs.

The catalytic performance of synthesized samples was tested by Suzuki-coupling reaction, which is a pioneering reaction to create C-C bonding. The result suggest that the KBM/Pd-ch possesses high activity in this field. The reusability of nanocatalyst was assessed and the result confirm after six cycle the efficiency just decreased about 3%, affirming good stability of nanocatalyst.

In the second section, Pd NPs was produced by LAL and deposited on the thin film of Graphene oxide (GO) deposited on stainless steel mesh by electrophoretic deposition (EPD). The nanocatalyst was characterized with different analysis and used in Suzuki- and Stille-cross coupling reaction.

Using carbon-based substrate to deposit NPs has garnered the attention due to its unique properties such as cost-effectiveness, accessibility and bio-friendly. Great attention has been paid to both GO and reduced graphene oxide (RGO) in chemical reactions as new types of auspicious supports or catalysts considering their high thermal/electrical conductivity, high surface area ( $\sim 2600 \text{ m}^2/\text{g}$ ), chemical stability, high loading capacity for metal NPs, easy recovery and recyclability among other excellent properties. In this regard, GO was chosen as bio-friendly substrate. Several types of deposition methods for GO coating are known, for instance, chemical vapor deposition (CVD), evaporation-assisted deposition (EAD), and electrophoretic deposition (EPD); the last one has garnered a lot of attention because of its cost-effectiveness and easy deposition, in a two-electrode cell filled with a suspension. To achieve effectual deposition, it is essential to have a stable suspension involving charge-free particles wherein an applied electric field moves the charged particles toward the opposite electrode and gather on the deposition electrode; such deposition of GO on different substrates with EPD and a uniform suspension of GO has been explored. These deposited electrodes can be used as substrates for nanoparticle deposition because of GO's porosity and its large specific surface area.

The EPD process has some parameters affecting the quality of thin film, such as concentration of GO, applied voltage, and deposition time. The mentioned parameters was optimized, to be more exact the mass differences before and after deposition was used as a gauge. Finally, the concentration, applied voltage, and deposition time were

adjusted 3 mg/mL, 25 V, and 10 min, respectively. The pre-synthesized thin film was then heated in vacuum oven at 100 °C for 2h and named mesh-GO. The wettability of mesh-GO has vital rule; therefore, the water contact angle (WCA) was measured about 45° confirming hydrophilicity nature of mesh-GO. The Pd NPs were deposited on mesh-GO using LAL and was carried out as follows: the mesh-GO was immersed in a cell filled with deionized water to hang the specimens. At the same time, the palladium target is placed at the bottom of the cell and to reduce the absorption of the laser wavelength, about 2 mm of water covers the whole target surface. The cell was kept under constant stirring using a stir plate, in a way that the magnet did not collide with the specimens and palladium target. As the LAL process was being performed, formation of Pd NPs in DI water and deposition of Pd NPs on mesh-GO were observed, simultaneously. In typical LAL as the ablation time increases the ablation rate decreases due to the absorption of the laser beam by colloidal NPs. Consequently, the preparation Pd NPs and their deposition on the surface of samples in one-step is advantageous; during laser ablation a portion of ensuing Pd NPs deposited on the mesh-GO surface. LAL was performed for about 3 min and when the laser ablation process was finished, stirring was continued for 5 min. LAL was performed for 15 min, just to prevent increasing the colloidal solution's temperature. The synthesized nanocatalyst was named mesh-GO/Pd.

The UV-vis spectroscopy was performed and the impulse of surface plasmon vibrations in the Pd NPs are around 250 nm. The UV-Vis results are in acceptable agreement with other available results. FT-IR spectroscopy affords a clear image of functional groups of the materials. The comparison of FTIR analysis represents that EPD process slightly reduced GO because of the decreasing intensity of Oxygen-containing functional groups. Loading Pd NPs on the surface of mesh-GO did not create a new vibrational

signal probably owing to the physical loading of Pd NPs. To visualize the specimens, SEM analysis was performed and the EDX spectrum was used to study the atomic percentage of samples. The SEM analyses of the mesh substrate, mesh-GO and annealed mesh-GO are presented; uniform GO deposited on the stainless steel mesh was apparent, and the EPD process succeeded in high quality deposition. Interestingly, the morphology of mesh-GO is the same as that of annealed mesh-GO, i.e. the annealing process did not affect the morphology of the sample. To study the Pd NP deposition influence on the morphology of mesh-GO, different magnifications of SEM images was provided. Throughout the images, the distribution of Pd NPs on the GO plate appears to be almost uniform, besides the deposition affecting sample porosity. The surface of the sample became slightly smoother when comparing with mesh-GO and annealed mesh-GO. To elucidate the chemical composition of mesh-GO/Pd, the EDX analysis was performed and result confirm presence of Pd NPs.

In this work, we report the use of mesh-GO/Pd as a new heterogeneous catalyst for the preparation of biaryls by C–C bond formation via Suzuki–Miyaura and Stille coupling reactions of halobenzenes with phenylboronic acid; excellent yields were obtained in most cases. The high activity about 97% was resulted in the presence of EtOH:H<sub>2</sub>O, K<sub>2</sub>CO<sub>3</sub>, and 0.07 g of nanocatalyst at 90 °C. The reusability of nanocatalyst provided compelling evidences for high stability; indeed, after 5 cycle the efficiency was decreased only 2%. The Stille- coupling reactions was studied by using mesh-GO/Pd and the excellent yields were obtained in most cases. Compared with literature examples of the Suzuki–Miyaura coupling reactions, the notable features of our work are:

- No expensive and toxic ligands are used
- Elimination of homogeneous catalysts and toxic organic solvents

- The use of the laser ablation in liquids (LAL) process as a fast, simple and clean synthetic route for the preparation of the Pd NPs
- High yields and short reaction times
- High reusability and stability of mesh-GO/Pd

The results presented here show the successful preparation and deposition of Pd NPs by laser ablation in liquids (LAL), via a protocol using GO/stainless steel mesh without using any chemical or capping agents. The synthesized sample was surveyed by EDX, SEM, UV-Vis and FT-IR spectroscopic techniques were used to characterize mesh-GO/Pd. The ensuing mesh-GO/Pd catalyst by the laser ablation process exhibits exceptional catalytic activity and good recyclability for Suzuki–Miyaura and Stille coupling reactions in benign EtOH : H<sub>2</sub>O.

In the third part, Laser ablation in liquid (LAL), one of the promising pathways to produce nanoparticles, is used herein for the modification of the abundant bio-waste, calcium lignosulfonate (CLS), adorning it with palladium nanoparticles (Pd NPs). The ensuing Pd/CLS nanocomposite, fabricated via a simple stirring method, is deployed for hydrogen storage and environmental cleanup studies.

It is universally known today that growing global pollution problems at an alarming rate are responsible for major irreparable damages to the environment. The rapid industrialization is liable for several environmental impacts on humans' life, such as climate change, water pollution, water scarcity, and unhealthy air, among others. Besides, depleting natural resources need to be envisaged as a sensitive matter. Meeting the society's demands requires alternative biofriendly and sustainable energy resources that do not contribute to much polluting emissions such as fuel cells. Hydrogen produced from water is one of the renewable energy forms that embraces this definition. Aiming for this sustainable target, the design and synthesis of novel materials in a



greener fashion from renewable and abundant resources has been the main objective. Among the bio-based materials, after cellulose, lignin is the most widely known naturally occurring biopolymer comprising of cross-linked amorphous copolymer bonded together by means of different C-O-C and C-C linkages. The ineptest characteristic of lignin would be impermeability, which possibly can be addressed by introducing various functional groups in lignin, sulfonation being more adaptable for application in industrial products. The enhancement of its water-soluble properties is the consequence of hydrophilic groups, such as sulfonate, phenolic hydroxyl, as well as alcoholic hydroxyl. In the presence of sulfonic groups, carbon chain, hydrophobic groups, along with hydrophilic groups, lignosulfonate (LS) shows good surface activity and acts as a catalyst. According to the production process deployed, diverse ion-based LS can be obtained as calcium, sodium, or magnesium lignosulfonates. LS, a three-dimensional network structured polyphenolic compound, can be simply oxidized electrochemically and makes an ideal substrate to decorate with nanoparticles thus modifying and fine-tuning its properties for high-end applications, namely, for energy storage and in catalysis.

Synthesis of nanocomposite-based materials for the hydrogen storage study has been one of the active research fields; nanocomposites encompassing nickel, palladium, platinum, and some metal oxide have the ability for hydrogen adsorption and desorption. Among these metals, Pd shows a unique ability for adsorption of hydrogen atom because of its structure, and adorning Pd NPs on such materials can turn them into effective catalysts for adsorption/desorption of hydrogen atoms and also reduction/degradation of environmental pollutants; such activity for hydrogen storage has been studied in nanocomposites, including Si wafer and single- and multiwalled carbon nanotubes.

CV is an acceptable method to study the electrochemical behavior of materials. In the present work, to investigate hydrogen adsorption/desorption, we applied CV tests to the CLS and Pd/CLS electrodes and also to the pure stainless-steel mesh, which is the substrate of the nanocomposite electrode. By applying potential in an alkaline solution, at first, water decomposition ( $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H} + \text{OH}^-$ ) was observed. This generated hydrogen tends to adsorb onto nanocomposites because of the electrode electric polarization under the applied potential. When the potential begins to decline, the liberated hydrogen atoms lead to recombination with  $\text{OH}^-$  to form  $\text{H}_2\text{O}$ .

Water contamination ensues when pollutants such as hazardous/toxic chemicals or biological agents and unwanted substances are introduced into water or wastewater which adversely affects the natural environment, quality of life and human health. Water contamination has become one of global problems that leads to different deadly diseases and disorders e.g. nervous system damage, diarrhea, skin irritation, typhoid, dysentery, polio and kidney failure. Discarded organic dyes effluent have been recognized as a serious threat to aquatic environments, humans, fauna and flora. Treatment of highly toxic organic/inorganic pollutants, especially pigments, organic dyes and heavy metals, from the environment and water/wastewater is not only vital, but also a global challenge for human health and industries. Consequently, it is essential to develop effective and facile strategies to remove and/or eliminate toxic/hazardous pollutants.

Introducing a new nanocomposite based on an abundant, renewable, and biofriendly material and utilizing a safe method to generate Pd NPs are the first aim of this section. The drop casting method was used to deposit pre-synthesized nanocomposites for hydrogen storage application. Additionally, nanocomposites were applied for reduction of Cr (VI) and 4-NP and degradation of MB.

In this section, to produce colloidal Pd NPs, a bulk piece of palladium was ultrasonically cleaned in distilled water and acetone. The Pd target is positioned at the cell bottom filled with deionized water. As the LAL process was performed, the color of deionized water turned black, affirming the presence of Pd NPs in deionized water. To prevent the agglomeration and reduce the rate of production for Pd NPs due to absorption laser beam by NPs, the LAL process was carried out in 3, 6, and 20 stages, each stage being of 5 min for Pd15/CLS, Pd30/ CLS, and Pd100/CLS, respectively. In each stage, 5 mL of deionized water was used in a way that about 2 mm water covers the whole target surface. After 5 min, the colloidal Pd NPs were extracted, and the LAL process, repeated with fresh deionized water. Finally, LAL was performed for different time periods: 15, 30, and 100 min. After the LAL process, CLS was added to the Pd NP colloidal solution and stirred with a magnetic stirrer for 24 h at room temperature. Finally, the ensuing nanocomposite was filtered and dried at ambient temperature in a dust-free atmosphere. According to LAL time, the nanocomposites were labeled Pdx/CLS, where x represents the ablation time ( $x = 15, 30, \text{ and } 100 \text{ min}$ ). The hydrogen storage performance was investigated by CV in 1 M KOH as electrolyte. The Ag/AgCl and Pt plate were used as reference and counter electrode, respectively.

The characterization of nanocomposite was completed by different analysis.

XRD pattern was studied crystallographically for the synthesized product. In addition, XRD was carried out to evaluate the influence of Pd NPs on the structure of Pdx/CLS. Subsequently, the XRD pattern of Pdx/CLS and Bragg's law were applied for estimation of the lattice parameter of Pd. Throughout the XRD pattern of CLS and Pdx/CLS, sharp peaks indicate that all synthesized samples are well crystallized. The strong and sharp peaks of CLS suggest that it exists as ultrathin nanosheets, which make an ideal space for loading of Pd NPs. The XRD pattern of Pd100/CLS shows two strong

reflection peaks at  $40.119$  and  $68.121^\circ$  associated with arrangement of (111) and (220) planes of Pd (JCPDS 46-1043). These diffraction peaks were assigned to Pd structure, thus confirming the successful formation of Pd100/CLS. When curves were meticulously compared, a significant decrease in intensity was observed around  $26.62$ ,  $29.3$ , and  $36.4^\circ$  owing to the immobilization of Pd NPs. Using XRD data and Bragg's and Scherrer's law led to estimate the lattice constant and crystalline size of nanocomposites. The comparison of results represent that increasing ablation time did not affect the crystalline size because of our unique method which is an obvious advantages. FTIR provides analysis to justify the presence of functional groups in the materials. The FT-IR spectra was recorded in the wavenumber range  $400$ - $3800\text{ cm}^{-1}$  for CLS and Pd100/CLS. The comparison of the spectrum of lignin and CLS shows the same main structural features of the samples. This is undoubtedly beneficial because the sulfonation did not alter the main structure and change just appeared in the lignin chains. The most characteristic infrared bands of CLS appeared at  $3000$ - $3500\text{ cm}^{-1}$  associated with the OH stretching. The spectrum of Pd100/CLS shows the same peaks as CLS. After immobilization of Pd NPs, there is not any significant peaks appeared due to physical loading of NPs. Admittedly, it must be mentioned that the intensity of peaks obviously decreased.

The surface structure is studied in terms of the adsorption/desorption  $\text{N}_2$  at  $77\text{ K}$  on the CLS and Pd100/CLS surface. The  $\text{N}_2$  adsorption/desorption isotherm of the samples, which suggests that the adsorption hysteresis loop in the  $P/P_0$  range is from  $0.7$  to  $0.99$ . This is likely due to the filling and draining of the mesopores by capillary condensation and usually attributed to bottleneck pores. While comparing  $\text{N}_2$  adsorption for CLS and Pd100/CLS, in the range of  $P/P_0 = 0.8$ - $0.99$ , a sharp increase of accumulation of  $\text{N}_2$  in the pores and the vacant space of Pd100/CLS becomes apparent. This leads to the

conclusion that Pd100/CLS has a large surface area because of the aggregated Pd NPs. The distribution of Pore diameter of the samples based on BJH theory was drawn as a function of pore diameter, the major peaks of CLS and Pd100/CLS were about 2.7 and 1.2 nm, respectively. BET results determined that surface properties of Pd100/CLS significantly increased in comparison with initial CLS. Interaction between Pd NPs and the surface of CLS leads to increase of mesoporous volume; consequently, the size and pore volume of CLS increased after Pd NPs' loading. The increasing surface area is probably due to the doping effect and the formation of new pores because of the loading Pd NPs on the CLS surface, and this enhancement of surface area and pore volume offers a good opportunity to adsorb and store hydrogen. The different magnification of SEM analyses for CLS nanocomposites depicting that CLS has a ravelike morphology with disparate porosity. It is envisaged that such a structure provides ideal space for attaching nanoparticles. The SEM images for Pd100/CLS confirmed the presence of Pd NPs on the CLS surface; Pd NPs appeared aggregated and did not show the regular morphology. To scrutinize the present Pd NPs on the CLS surface, TEM analysis was performed for Pd100/CLS. Light gray thin films are CLS nanosheets interconnected in a disorderly arrangement, as corroborated by another report. Spherical type structures were formed in some regions, indicating that Pd NPs aggregated with each other, the space between Pd NPs and CLS surface being the generated porosity. The average diameter of Pd NPs is estimated, with Image J software, to be about 8 nm. These results are in acceptable agreement with the BET and SEM analysis. SEM image of the ensuing electrodes depicts rough structures offering easy access of active sites at the surface between electrodes and electrolyte medium. The elemental attendance was assessed by EDX analysis and the results confirm the presence of Pd NPs in the nanocomposite.

To comprehend the electrochemical conduction of samples, CV study was performed in a three-electrode cell filled with 1 M KOH at a sweep rate of  $50 \text{ mV s}^{-1}$  using a stainless-steel mesh substrate deposited with CLS and Pd100/CLS. According to the CV curves, the results suggest that the mesh substrate has no evident peaks in this potential window; i.e., it does not adsorb and desorb hydrogen. In contrast to stainless-steel mesh, the CV curve of CLS shows minor faradic peaks, which means that the CLS can adsorb and desorb a little hydrogen. To take into account Pd NPs' performance in adsorbing and desorbing hydrogen, the CV curve of Pd15-100/CLS was compared to CLS. As apparent, all curves show oxidation and reduction peaks, demonstrating that hydrogen was adsorbed and desorbed on the surface of the working electrodes. In the cathodic direction, in the scan to negative potential, the CV curve of Pd15-100/CLS shows a reduction peak (C) due to water decomposition, H formation, and adsorption at the electrode surface. In contrast, in the anodic direction, an oxidation peak (A) shows hydrogen desorbing on the surface of Pd15-100/CLS electrode, due to the faradic reaction. The reduction peak is associated with hydrogen adsorption on the Pd surface. The produced hydrogen was adsorbed and stored on the surface of the working electrode due to the polarization created by the applied potential. These potential peaks, in the cathodic and anodic process, show a quasireversible electrochemical reaction appearing on the Pdx/CLS electrodes. To assess the influence of Pd NPs in hydrogen adsorption/desorption, the oxidation and reduction peak currents are compared. The results show that immobilization Pd NPs on CLS has a meaningful effect on the oxidation and reduction peaks, thus emphasizing that Pd is an effective catalyst for hydrogen adsorption and desorption. The Pd100/CLS possesses high activity compared to others and was selected as a best electrode.

The stability of electrode during cyclic voltammetry is a necessary parameter. This parameter was investigated by CV during 100 cycle. The amount of hydrogen desorbed can be measured by the integration of the anodic peak. The total charge related to hydrogen desorption can be associated with the integral of the curve where atoms are being desorbed. Given that the electrode/electrolyte interface act as a capacitor, the measurement of  $Q_H$  is done by assuming a baseline to separate the double layer and faradic region. To investigate the cyclic life performance of Pd100/CLS, a CV curve for 100 cycles was obtained.  $Q_H$  was estimated and drawn as a function of the cycle's number. As the result shows, the amount of hydrogen charge decays with the increase in the cycle number. In the first 20 cycles, a 43% decrease in  $Q_H$  is probably due to the oxidation of the electrode;  $Q_H$  decrease during scans maybe due to the separation of Pd100/CLS from the electrode surface.

Catalytic study of nanocatalysts were investigated by Cr(VI) and 4-NP reduction and MB degradation. The Cr(VI) and 4-NP reduction by Pd100/CLS shows high activity compared to pure CLS, confirming the rule of Pd NPs in this application. The MB degradation was completely achieved after 1 s by using Pd100/CLS. The reusability of Pd100/CLS was comprehended through Cr(VI) reduction, the results show the activity of Pd100/CLS after 8 cycle was decayed about 3%.

In the forth section, hydrogen production was achieved by water splitting by Bismute vanadate (BV) modified with phosphorus doped graphitic carbon nitride nanosheets (PCNS) by photoelectrochemical method.

Among multitudinous semiconductors,  $\text{BiVO}_4$  has been dedicated as one of the foremost semiconductor in PC and PEC water splitting due to its suitable band gap ( $\sim 2.4$  eV) and the position of band edges. Admittedly, it must be considered that  $\text{BiVO}_4$  has some drawbacks such as poor charge separation and fast charge

recombination, which could restrict its efficiency. To overcome these shortcomings, different efforts have been dedicated such as morphological engineering, elemental doping, introducing co-catalysts, and combining with other semiconductors. Formation of heterostructure system with different semiconductors can boost separation and transportation of charges; consequently, the higher performance is provided down to the more participating of charges in appropriate regions. Compared to others, GCN has been recommended as a pioneering metal-free polymeric semiconductor owing to its advantageous such as nontoxicity, moderate band gap (2.7 eV), and suitable band edge. According to reports, getting rid of this obstacle could be achieved by turning the bulk of GCN into ultrathin nanosheets. Although ultrathin nanosheets of GCN offer intriguing advantages but its large band gap limits practical application for solar light absorption. In the quest for a solution, the most successful way to confront this handicap would be engineering electronic structure by elemental doping, which provides the enhancement of light absorption, facilitating charge transfer mobility, and forming new active sites. Phosphorus doping has been suggested for increasing surface area, decreasing band gap energy, improving electrical conductivity and restraining charge carrier recombination.

Present work emphasized on the modification of  $\text{BiVO}_4$  by adding phosphorus doped graphitic carbon nitride nanosheets (PCNS) to evaluate the photoelectrocatalytic performance by forming Z-scheme heterojunction. The photoanodes were fabricated by trustworthy solution combustion method recommended as a feasible route. To elucidate the impact of surface area, the performance of bulk and nanosheets of GCN was compared. A clear view of the influence of phosphorus doping was provided by the comparison of photoanodes with or without phosphorus. Afterwards, the effect of PCNS portion and concentration per  $1 \text{ cm}^2$  on PEC performance was assessed. The



electrochemical impedance spectroscopy (EIS) was used to investigate charge transferring resistance. The stability of the optimized photoanode was cautiously studied over days.

The nanocomposite structural properties was evaluated by XRD analysis and results affirmed the PCNS was well synthesized. The presence of phosphorus led to the positive shift of peak's position due to larger radius of P compared to C. Comparison the FTIR spectrum confirmed P doping did not alter the chemical functional group. The BET analysis shows turning CNB into CNS increased the specific surface area and it decreased after P doping but it is higher than CNB. The FESEM presents the packing order of nanosheets and EDX confirmed presence of C, N, and P atoms in nanocomposite. The optical features was analyzed by DRS and PL and the bandgap was calculated by Tauc plots. The absorption edge of PCNS was shifted to higher wavelength and the bandgap was declined about 2.35 eV, also comparison PL spectra of CNS and PCNS shows the recombination rate was declined by P doping. The XRD of BV and BV-PCNS was affirmed the  $\text{BiVO}_4$  was synthesized in monoclinic structure. Morphological investigation was done by FESM and the results shows BV and BV-PCNS was fabricated in porous structure provided more channels to charge carrier movement; additionally, the presence of P atom in BV-PCNS was confirmed by EDX analysis. The survey of the water splitting performance of photoanodes including BV, BV-CNB, BV-CNS, and BV-PCNS was completed by PEC method under 1 sun illumination. The linear sweep voltammetry (LSV) shows the BV-PCNS achieved high photocurrent density along with low onset potential, this phenomenon was explained by high surface area and lowest charge recombination rate of PCNS compared to CNB and CNS, respectively. The charge transfer resistance was elucidated and the results show the lowest resistance is belong to BV-PCNS. The

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optimization of weight ratio of PCNS into  $\text{BiVO}_4$  suspension is important and was achieved by introducing different weight of PCNS. The LSV and CV results presented BV-PCNS2 possesses the highest photocurrent density and electrochemical surface area. The charge transfer resistance was assessed by EIS analysis and the fitting results shows the better charge transfer was provided by BV-PCNS2 implying the optimum weight ratio accelerates charge carriers movement as well as hinders charge recombination. Providing the better performance, BV-PCNS2 was chosen to optimize the amount of dropped suspension ( $40\text{-}80\ \mu\text{L}/\text{cm}^2$ ) on ITO substrate. The LSV was performed and photocurrent density at  $1.23\ \text{V}$  vs. RHE was measured as a gauge. The better result was accomplished by BV-PCNS2-50, confirmed the thickness of thinfilm matters due to its influence on harvesting light ability. The LSV test was done during different days (21 calendar days) and comparison of results shows that the photoelectrochemical activity of BV-PCNS-50 was declined about half-fold compared to the first run.



Bu-Ali Sina University  
Dissertation Information

**Title:**

Synthesis of palladium nanoparticles via chemical and laser ablation methods and its usage to produce nanocomposites based on polyethylene, Graphene Oxide and lignin and evaluation its applications

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**Department:** Physics

**Subject:** Physics

**Field:** Atomic and molecular physics

**Degree:** Ph.D

**Approval Date:** 2019-6-10

**Defence Date:** 2021.7.20

**Number of Pages:** 177

**Abstract:**

In this work, a simple and cost-effective process for the fabrication of palladium nanoparticles (Pd NPs) with laser ablation in liquid (LAL) method was suggested. Pd NPs were deposited on the bio-friendly materials and the results affirmed LAL was managed to fabricate Pd NPs. In the first section, Pd NPs were fabricated by LAL and chemical reduction; then were deposited on polyethylene by a simple magnetic stirring. Pd NPs was more uniformly distributed on the substrate by chemical method, the catalytic investigation, Suzuki reaction, confirmed the nanocatalyst possesses high catalytic activity (96%) and stability during several usage. In the second section, the Pd NPs were fabricated by LAL and deposited on the thin film of Graphene oxide (GO), which was deposited on stainless steel mesh by electrophoretic deposition. The Suzuki reaction investigation exhibited high catalytic activity (97%) and stability of nanocatalyst during six run. In the third section, Pd NPs preparation was done by LAL and immobilization on the surface of Calcium lignosulfonate was achieved by stirring method. The pre-synthesized nanocomposites was utilized to study hydrogen production and the results suggest the current of anodic peak for the best electrode is raised about 43-folds compared to bare substrate. Catalytic performance of synthesized nanocomposites was surveyed by the reduction of Cr(VI) and 4-NP and the degradation of MB, the results suggested high efficiency performance about of 100%. In the fourth part, water splitting by BiVO<sub>4</sub> modified by phosphorus doped g-C<sub>3</sub>N<sub>4</sub> nanosheets was surveyed. The results affirmed presence of PCNS led to increasing photocurrent density about 5-folds compared to bare BiVO<sub>4</sub> which is courtesy of boosting life time and density of charge carriers and decreasing of charge resistance transformation.

**Key Words:** Palladium nanoparticles; Laser ablation; Graphene oxide, Polyethylene; Calcium lignosulfonate; Suzuki reaction; Hydrogen storage, Bismute vanadate, Carbon nitrid, water splitting.



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**Thesis Submitted in Partial Fulfillment of the  
Requirements for the Degree of Ph.D in Atomic and molecular physics**

**Title**

**Synthesis of palladium nanoparticles via chemical and laser ablation  
methods and its usage to produce nanocomposites based on polyethylene,  
Graphene Oxide and lignin and evaluation its applications**

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**July, 20, 2021**