

Production of Hydrogen by Water Splitting Using Synthesized Porous Pt-Pd Nanodendrites for Energy Applications

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Abstract

The continual increase in world population and lifestyle standards has led to a seminal growth in global energy consumption amounting to about 90% of global energy as fossil fuels supply the transportation and industrial sectors. This led to high emission of greenhouse gases including carbon dioxide, resulting in a substantial depletion of carbon-based resources that could be otherwise used to produce valuable chemicals. In 2013, worldwide energy consumption was 17 TW and is expected to at least double by 2050. This research studied the rational design of porous binary Pt-based nanodendrites as an efficient catalytic system for electrochemical driven water splitting for energy production. Porous Pt-Pd nanodendrites were typically synthesized by the reduction of the metal precursors by L-ascorbic acid (AA) in the presence of PVP as a structure-directing agent under ultrasonication. The Platinum-Palladium (Pt-Pd) was used as a catalyst in water splitting technique for hydrogen production and compared with commercial Pt/C catalyst. Several tests were done on the samples including Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV), IT, ET to measure the energy rate and the characterization at the last step.

Keywords

catalyst, fuel cell, porous, platinum, nanodendrites, sonication

1. Introduction

The preparation method of porous Pt- based nanostructured materials possess intriguing physical, chemical properties and morphology generating promising potential for important applications like fuel cells, sensors, stimulation electrodes, mechanical actuators, and catalysis [1]. With the advances of fabric science and nanotechnology, porous Pt- based nonmaterials with well-controlled composition, shape, and geometrical configuration are rationally designed and fabricated. Importantly, their superior properties including unique pore structure, large specific expanse and excellent structural stability have fuelled up great interest to boost their current performance and to explore new applications [4-7]. The correlations between the composition and morphology of the catalysts and their catalytic properties are discussed based on some important and representative examples. In the development of water splitting, the sluggish electrocatalytic kinetics of the Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER) have restricted their energy conversion efficiencies. Along with the continuous rise in the prices of noble metals and transition metals (such as cobalt and nickel), constructing high-efficiency HER/OER catalysts based on low cost transition metals, such as iron and manganese, is becoming more meaningful in developing industrialized water splitting devices. Although the possibility of water photolysis has been investigated by many workers, a useful method has been developed. Because water is transparent to visible light it cannot be decomposed directly, but only by radiation with wavelengths shorter than 190 nm. However, semiconductor photocatalysis has received much attention as a potential solution to the worldwide energy shortage and for counteracting environmental degradation [8-10]. Photocatalysis technology has received much attention in recent years because of its outstanding

performance to degrade a wide range of toxic compounds under solar irradiation, which greatly reduce environmental problems. Photocatalysis is a promising technique for biodegradation and pollution control. Over the years, research has been conducted using a whole series of materials as photocatalysts for the purpose of organic decomposition and degradation of other wastes. Photocatalysis involves oxidation and reduction reactions with the help of photo-emitted charge pairs under visible light [11].

1.1. Water splitting

Water splitting is the chemical reaction in which water is broken into oxygen and hydrogen. Efficient and economical photochemical water splitting would be a technological breakthrough that could underpin a hydrogen economy. No industrially practical version of water splitting with pure water has been demonstrated, but the two component reactions (H_2 production and O_2 production) are well known. The water splitting of seawater and other salt water is used industrially to make chlorine. However, the waste hydrogen collected comprises about five percent of the world's supply. A version of water splitting occurs in photosynthesis, but hydrogen is not produced. The reverse of water splitting, Figure 1, is the basis of the hydrogen fuel cell. Hydrogen is known to have the potential to become an important source of energy.

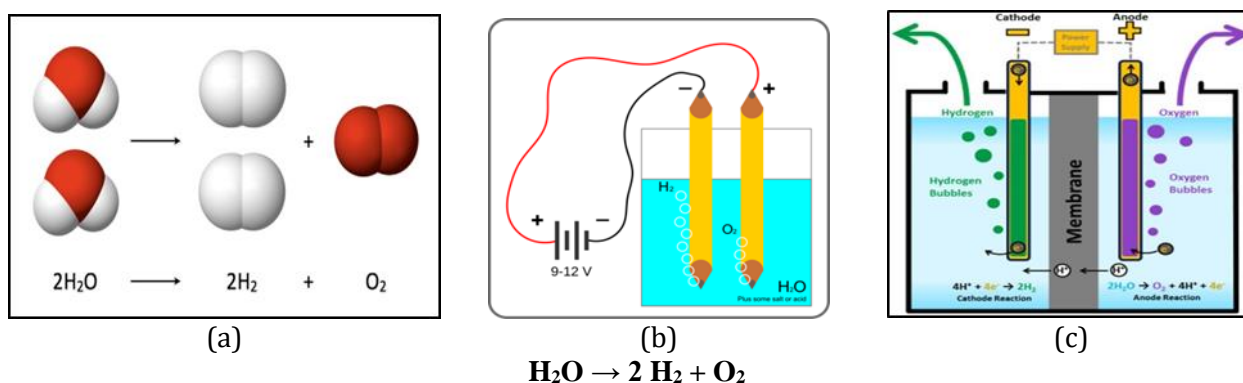


Fig. 1. Water splitting [2]

1.2. Platinum (Pt) is as catalyst?

Cars are equipped with catalysts to disarm toxic exhaust gases. Platinum plays an important role there. Leiden physicists and chemists have now for the first time seen the mechanism behind a platinum catalyst. With a fundamental understanding Pt-based dendrites the Platinum and platinum alloys are the most efficient catalysts for speeding up chemical reactions in hydrogen fuel cells. At the cathode, oxygen molecules combine with electrons and hydrogen ions to form water. This reaction is sluggish and speeding it up requires 10 times as much platinum as is used at the anode process, scientists can use this rare material more efficiently due to the growing demand for energy and impending environmental issues. Fuel cells have attracted significant attention as an alternative to conventional energy technologies. As cost is the main inhibitor of this technology, low-cost catalysts with high activity and stable catalytic performance are the key to large scale application of fuel cells. Discussion is mainly focused on the structure and composition of Pt and Pt-based electrocatalysts, which significantly affect the catalytic activities and durability of fuel cell catalysts. Various form of Pt has been used in fuel cells including Pt single metal, Pt-based alloys (including noble alloys, non-noble alloys, metal oxide alloys, and non-metal alloys, and structure-controlled alloys (nanopolyhedra, Nanodendrites and hollow and core-shell structures) [13, 14].

1.3. Pt based nanodendrites for water splitting

Precise fabrication of porous ternary Pt-based nanodendrites is very important for electrochemical energy conversion owing to high surface area and great molecular accessibility of these nanodendrites. Porous Pt-Pd nanodendrites were typically synthesized by the reduction of the metal precursors by L-ascorbic acid (AA) in the presence of PVP as a structure-directing agent under ultrasonication. Briefly,

0.06 g of PVP is mixed with 5 ml of an aqueous solution containing 3 ml of Na_2PdCl_4 (50 mM) and 3 ml of K_2PtCl_4 (50 mM). Then, 6 ml of AA (0.1 M) were quickly added under sonication and kept under sonication for an additional 1 hour at room temperature before consecutive centrifugation/washing cycles at 10,000 rpm for 20 min using DDI water and then kept for further characterization (Figure 2) [14, 15].

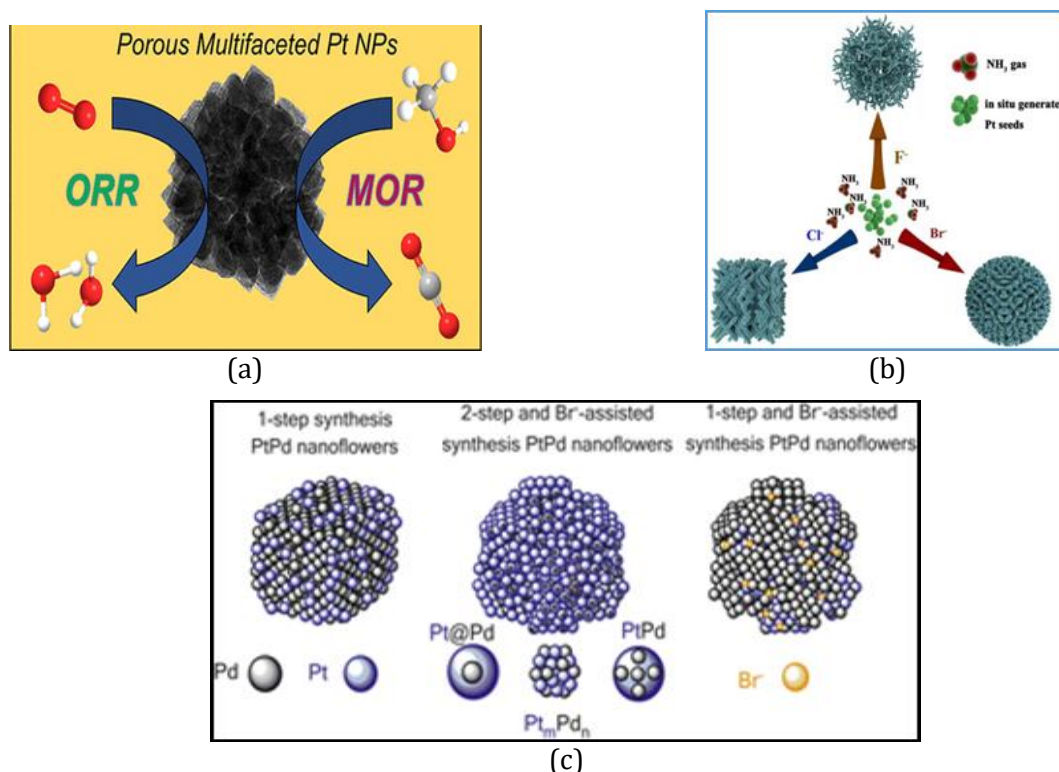


Fig. 2. Pt based nanodendrites

- (a) porous Pt-based nanodendrites; (b) structural characterizations of the porous Pt nanodendrites with NH_4F as regulating reagent under NH_3 atmosphere [1];
(c) Pt-Pd nanodendrites and their superior electrocatalytic activity [3]

As with platinum, the palladium-catalyzed oxidation of anomeric hydroxyl groups in aldoses is a rather selective process. The influence of pH in the Pd-catalyzed oxidation of glucose has been studied. It was observed that the Glucuronic acid formed, in its free form, reversibly inhibits the oxidation process in acidic media. The oxidation of d-glucose has been performed with palladium-on-alumina and bismuth-containing palladium-on-charcoal in water. The selectivity in the air oxidation of aqueous d-glucose and d-gluconate has also been examined, with Pt catalysts supported on activated charcoal, with or without such promoters as bismuth or gold. The combined use of such heavy metals as bismuth, together with Pt or Pd, introduced an important improvement in the selectivity of these catalytic oxidations. Thus, the use of Pd, or both Pd and Pt catalysts, doped with bismuth, led to an enhancement in the selectivity of the oxidation. An additional advantage of these catalysts is that their susceptibility to poisoning by molecular oxygen is strongly diminished, making the oxidations more efficient. These processes are useful for the oxidation of d-glucose and various mono-di and oligo-saccharides on the industrial scale [16, 17].

1.4. Importance of the Pt-Pd catalyst

Controlled design of Pt-Pd nanodendrites ornamented niobium oxynitride nanosheets for solar-driven water splitting has been studied by Alotto et al. [5]. The later efficient photocatalysts for the water splitting reaction is crucial in a fuel cell reaction presenting a facile roadmap for one-pot fabrication of Pt-Pd nanodendrites (ND) ornamented niobium oxynitride nanosheets (PtPd/NbON) for solar-driven water splitting.

This was achieved by annealing Nb₂O₅ under NH₃ to form Niobium oxynitride (NbO) nanosheets which were subsequently used as starting seeds for the simultaneous growth and self-assembly of Pt-Pd NDs with the assistance of Plutonic F. The water oxide performance of Pt/Pd/NbON was substantially superior to those of NbON and Nb₂O₅. This is ascribed to the combination of NbON with its great visible-light-harvesting properties and narrow band gap and the unique catalytic merits of PtPd NDs. Exploiting high-efficiency and low-cost bi-functional electrocatalysts for the Hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) has been actively encouraged because of their potential applications in the field of clean energy [18].

Conducting polymer alloys for photo-enhanced electro-catalytic oxygen reduction Electro-catalysis is a core element in many technologies proposed for energy storage and conversion in a post-petroleum energy landscape. This has prompted the development of new electro-catalysts, for example for fuel-cells, water-splitting cells, and metal-air batteries, which are not based on traditional rare metals such as platinum, palladium and iridium. In this context, the possibility to use organic conjugated polymers to replace inorganic catalysts has shown promising progress. It is demonstrated that an "alloy" of two conjugated polymers, poly[3,4-ethylenedioxythiophene] and polythiophenes, with different oxidation states can act as a photo-enhanced reduction catalyst for the oxygen reduction reaction and thereby reduce the over potential for that reaction by more than 600 mV under illumination [5, 19].

A series of well-dispersed bimetallic Pd-Pt nanodendrites uniformly supported on XC-72 carbon black are fabricated by using different capping agents. These capping agents are essential for the branched morphology control. However, the surfactant adsorbed on the nanodendrites surface blocks the access of reactant molecules to the active surface sites, and the catalytic activities of these bimetallic nanodendrites are significantly restricted. In this research, a facile reflux procedure to effectively remove the capping agent molecules without significantly affecting their sizes is reported for activating supported nanocatalysts. More significantly, the structure and morphology of the nanodendrites can also be retained, enhancing the numbers of active surface sites, catalytic activity and stability toward methanol and ethanol electro-oxidation reactions. The as-obtained hot water reflux-treated Pd-Pt/C catalyst manifests superior catalytic activity and stability both in terms of surface and mass specific activities, as compared to the untreated catalysts and the commercial Pt/C and Pd/C catalysts. We anticipate that this effective and facile removal method has more general applicability to highly active nanocatalysts prepared with various surfactants and should lead to improvements in environmental protection and energy production [20].

1.5. Nanodendrites of Platinum-group metals for electrocatalytic applications

Developing highly efficient and sturdy catalysts for future electrochemical and energy applications is one amongst the most subjects of the many studies in renewable energy generation. Within the past several years, researchers have developed Pt-based alloy electrocatalyst nanomaterials that exhibit promising electrocatalytic properties for various electrochemical applications. The efficient structural and morphological control of Pt-based alloy materials plays a decisive role in achieving these enhanced electrocatalytic properties. The oxygen evolution reaction (OER), hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and methanol oxidation reaction (MOR) are of particular interest; thus, investigation of the event of active and sturdy catalytic materials for these electrochemical processes is required Pt-group metals (PGMs) and their alloys have emerged because the most active electrocatalysts.

The six noble transition metals (Pt, Pd, Rh, Ru, Ir, and Os) in groups 8–10 (VIII) of the periodic utilization efficiency of PGMs, significant efforts are made to style and synthesize multi-metallic alloy electrocatalysts. The alloying of two or more metals is an efficient strategy to enhance the cost-effectiveness and catalytic performance, because Pt-based multi-element catalysts are often superior to monometallic Pt nanostructures due to the possible synergistic effects between Pt and other elements.

The electrochemical properties of nanostructured alloys depend upon their sizes and morphologies. Therefore, recent developments have led to the formation of assorted shapes and structures of the alloy electrocatalysts to boost the electrocatalytic activity and stability. Furthermore, dendritic structures can

show high electrocatalytic activity attributable to the proportion of catalytically active atoms at the sting and corner, which may provide abundant catalytic sites and sufficient absorption sites for molecules involved within the reactions of interest [21, 22].

1.6. Dendritic Pt nanostructures

The synthesis of nanostructured Pt catalysts with a large surface area and well-controlled size and shape, such as dendritic Pt nanostructures, is of great interest for achieving high electrocatalytic performance. Developed a synthetic method for spherical Pt nanodendrites, which consists of the seeding and autocatalytic reduction of Pt salts in the presence of surfactants using AA as the reductant. The final shape of the Pt nanostructures was found to be solely dependent on the size of the employed liposomes. The obtained Pt nanodendrites were found to be suitable for photocatalytic hydrogen evolution from water [23].

1.7. Dendritic Nanostructures for Electro Catalysis

Thus far, numerous alloys and composites based on PGM dendritic-like structures have been reported for electrochemical applications. The rich edges and corner atoms present in the dendritic structure make them promising and desirable electrode materials. Because the shape, dimensionality, and composite structure of Pt have a considerable influence on the electrocatalytic behaviour, a discussion of the various nano-dendritic structures of PGMs, particularly the electrocatalysts, is presented in the following subsections [24].

1.8. Dendritic Pd nanostructures

Considering the economic viability of noble-metal-based electrocatalysts, it is essential to reduce the fabrication and production costs by greatly improving the performance and durability of non-Pt catalysts. Non-Pt catalysts, such as Pd, can be a good substitute for Pt because they are often more abundant than Pt but have comparable electrocatalytic properties. Despite the interesting electrocatalytic properties of Pd nanostructures, they have been less extensively studied than Pt [25].

1.9. Dendritic Pt-Pd nanostructures

The morphology of the Pd seeds and the corresponding exposed facets were found to have a great influence on the nucleation and growth of the deposited Pt metal, which determines the catalytic properties of the dendritic nanostructures. Compares the morphology and the surface area of commercial Pt/C and Pd-Pt dendrites, the dendritic structure shows high-index exposed facets. The specific electrochemical surface area (ECSA) of the Pd-Pt dendrites is 77% of the commercial Pt/C, which is a reasonable [26-29].

1.10. Hydrogen energy evolution reaction (HER)

The HER is of prime importance in clean energy production and is a sustainable, zero-C-producing method. Although commercial Pt/C catalysts show remarkable electrocatalytic performance for the HER, further stability enhancement is required because of the poor durability during the electrocatalytic reaction. The nanodendritic structure of platinum-group minerals (PGM) alloys makes them suitable candidates for enhancing the stability and electrocatalytic activity. Wang et al. [33] demonstrated the enhanced HER stability of AuPt dendrites in acidic conditions. While the overpotential of AuPt dendrites was slightly increased, compared with that of commercial Pt/C, the long-term stability was dramatically enhanced. Furthermore, nanohexapods comprising Pt, Ni, and Co exhibited exceptional enhancement of the intrinsic electrocatalytic activity towards the acidic HER.

Recently, the shape- and size-controlled synthesis of noble-metal-based electrocatalysts for energy applications has attracted tremendous research interest. This is demonstrated by the increasing number of publications over the last decade concerning noble metal-based nanostructures of diverse sizes, shapes, and morphologies. While many of the previously published review papers focused on the recent developments in metal electrocatalysts, this review places a spotlight on PGM nanodendrites and their electrochemical properties [30-33].

2. Materials and Methods

2.1 Materials

K₂PtCl₄, Na₂PdCl₄, L-ascorbic acid (AA); poly (vinylpyrrolidone), a commercial Pt/C (20 % Pt), HClO₄, and KOH were purchased from Sigma-Aldrich Chemie GmbH (Münich, Germany) commercial Pt/C catalyst E-TEK Pt/C (20 wt % of 2-5 nm Pt nanoparticles on Vulcan XC-27 carbon support) was obtained from alfa aesar. All chemicals were used as received.

2.2. Method of electrochemical water splitting

All electrochemical measurements were conducted in a conventional three-electrode glass cell using a Gamry electrochemical analyzer (3000, Gamry Co., USA). A platinum wire, saturated calomel electrode (SCE), and glassy carbon electrode (GCE, 5 mm diameter) were used as the counter, reference and working electrodes, respectively. The GCE was coated with 16 µg of each catalyst and 10 µl of Nafion (0.05 %), followed by drying at 80 °C before the electrochemical measurements. Prior to each measurement, 200 cyclic voltammograms (CVs) cycles were performed to clean the GCE in N₂-saturated different electrolytes including HClO₄, NaOH, and PBS solutions at a scan rate of 100 mV/s [35]. The Electrochemical Surface Area (ECSA) was calculated as [34]:

$$\text{ECSA} = Q_{\text{H}}/m \times 210,$$

where Q_{H} is the charge for (Potential-dependent Gibbs reduction energies) H_{upd} adsorption determined as

$$Q_{\text{H}} = 0.5 \times Q,$$

where Q is the charge in the H_{upd} adsorption/desorption area obtained after the double layer correction region, m is the loading amount of Pt on the GCE, and 210 µC/cm² is the charge required for monolayer adsorption of hydrogen onto Pt surface.

All the measured current densities were normalized in reference to the geometric area of GCE, while all potentials were recorded with IR-drop correction. All measurements including linear sweep voltammograms (LSV), cyclic voltamogram (CVs), emepidence (EIS), chronoamperometry (CA), and chronopotentiometry (CP) were conducted in N₂- [7, 35-39].

2.3. Materials characterization

The size, morphology, and composition of the synthesized NCs were investigated using a transmission electron microscope (TEM) (Tecnai G220, FEI, American) equipped with a high-resolution TEM (HRTEM), energy dispersive X-ray (EDX), and high-angle annular dark-field scanning TEM (HAADF-STEM) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) spectra of different nano-catalysts were recorded by a Kratos AxisUltra XPS spectrometer equipped with a monochromatic Al Kα radiation source (1486.6 eV) under UHV environment (cca. 5×10⁻⁹ Torr). X-ray diffraction pattern (XRD) was recorded on an X'Pert-Pro MPD diffractometer (P Analytical Co., Netherlands) using Cu Kα X-ray source (λ = 1.540598 Å). The inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to determine the catalyst loading amount onto the GCE.

2.4 Electro catalytic water splitting reaction

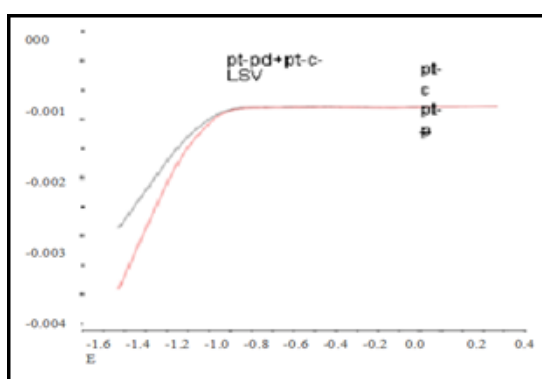
Recently as a promising strategy to convert and store solar energy in the form of chemical energy there are three artificial photosynthesis schemes: direct hydrogen fuel production through water splitting, direct carbon-based fuel production, and indirect carbon-based fuel production. In each of the three schemes, the only remnants following consumption of the produced fuels are the water (H₂O) and carbon dioxide (CO₂) used to produce them. Thus, all three schemes are self-sustainable and carbon-neutral [40-42].

3. Result and Discussion

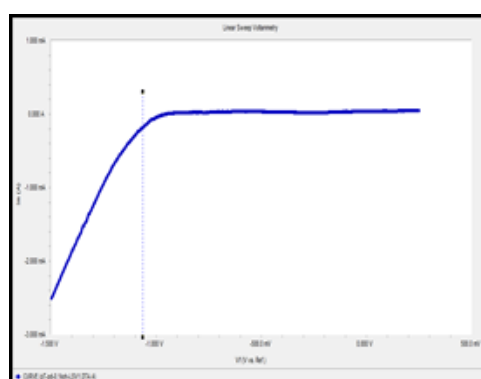
3.1. Linear sweep voltammetry

LSV, see Figure 3, is an essential analytical method for evaluating electrode performance; however, it has not been firmly established yet in the MEC field. Linear sweep voltammetry (LSV) is a simple electrochemical technique. The method is similar to cyclic voltammetry, but rather than linearly cycling

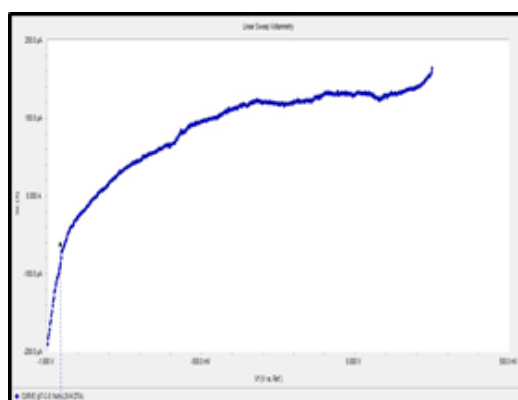
over the potential range in both directions, linear sweep voltammetry involves only a single linear sweep from the lower potential limit to the upper potential limit. Like cyclic voltammetry, linear sweep voltammetry uses a three-electrode system. This consists of a working electrode, counter electrode, and reference electrode. The three electrodes are connected to a potentiostat and are placed in an electrochemical cell along with the solution of interest. The potentiostat controls the potential between the working electrode and reference electrode and measures the current at the counter electrode so that a plot of potential vs. current can be made. This shows the electrochemical response (oxidation or reduction) of the material in question. A peak or dip can be seen at the potential where oxidation or reduction begins. Linear sweep voltammetry can be used to calculate the peak current, calculate the peak current potential, and calculate the half-peak current potential. For irreversible systems, linear sweep voltammetry is a simple and effective alternative to cyclic voltammetry.



(a) Pt-Pd + Pt/C



(b) Pd-Pt LSV



(c) Pt-Pd LSV

Fig. 3. Linear sweep voltammetry (LSV)

3.2. Cyclic Voltammetry test

Cyclic Voltammetry test (CV), Figure 4, is an electrochemical technique for measuring the current response of a redox active solution to a linearly cycled potential sweep between two or more set values. It is a useful method for quickly determining information about the thermodynamics of redox processes, the energy levels of the analyte and the kinetics of electronic-transfer reactions. Like other types of voltammetry, cyclic voltammetry uses a three-electrode system consisting of a working electrode, reference electrode, and counter electrode. To perform cyclic voltammetry, the electrolyte solution is first added to an electrochemical cell along with a reference solution and the three electrodes. A potentiostat is then used to linearly sweep the potential between the working and reference electrodes until it reaches a pre-set limit, at which point it is swept back in the opposite direction. This process is repeated multiple times during a scan and the changing current between the working and counter probes is measured by the device in real time. The result is a characteristic duck-shaped plot known as a cyclic voltammogram, see Figure 4 and Table 1.

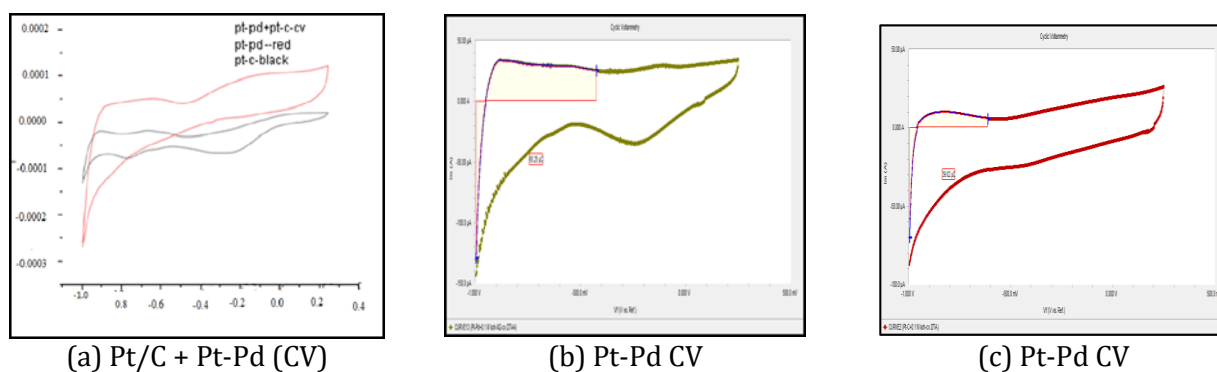


Fig. 4. Cyclic Voltammetry Test (CV)

Table 1. The CV and LSV of Pt/C and Pt-Pd

	CV	LSV
	Q	E
Pt/C	39.02	-960
Pt-Pd	65.25	-1.075

From the above Table 1, and Figures below, it is found that when using the Pt-Pd the Q was higher than Pt/C. That means we will get more energy in the case of using Pt-Pd as a catalyst than in the case of Pt/C. This is evident from the energy produced as calculated by the equation below:

$$\begin{aligned}
 \text{Pt/C:} \quad & E = Q_H / (M \cdot 210); \quad Q_H = 0.5 \cdot Q \\
 & Q_H = 0.5 \cdot 39.02 = 19.51 \\
 & E = 19.51 / (26 \cdot 210) = 0.00357 \\
 \text{Pt-Pd:} \quad & E = Q_H / (M \cdot 210); \quad Q_H = 0.5 \cdot Q \\
 & Q_H = 0.5 \cdot 65.25 = 32.6 \\
 & E = 32.6 / (26 \cdot 32.6) = 0.0384
 \end{aligned}$$

3.3. Transmission Electron Microscope

Referring to the images of TEM, Figure 6, it is found that the best shape, size and composition in the Pt-Pd at as low as 20 nm for Pt-Pd proving a nano size structure Pt-Pd. The Pd-Pt and other catalysts at a nano scale show excellent HER catalytic activity. Characterization results reveal that there are a great deal of surface hydroxyl groups or oxygen vacancy on the surface of Pd-Pt catalyst [43].

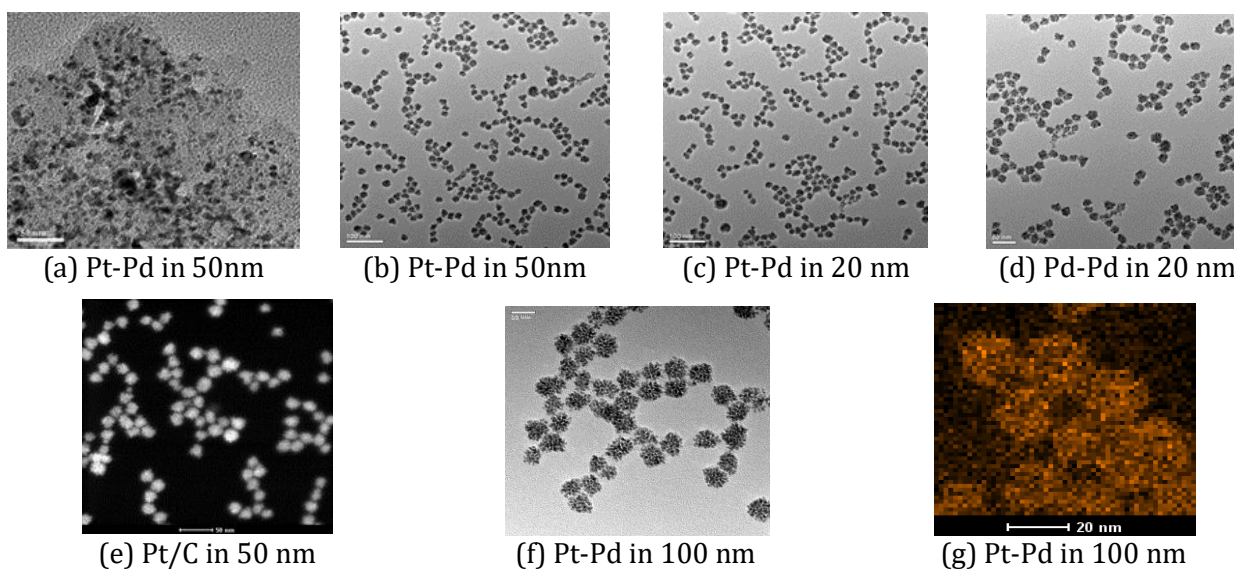


Fig. 6. The transmission Electron Microscope image of Pt-Pd and Pt/C nanodendrites

3.4. XRD and EDX results

The peaks of the XRD pattern play a vital role in the identification of the phases as well as the properties of the nanoparticles. In this case, the width of the peak would reveal the average crystalline size of the nanoparticles where sharp peaks indicate a large size of crystallites, whereas broad peaks indicate smaller crystallites. This clear in this case Pd and Pt as in Figure 7 where a nano size particle is proved to be present enhancing the photocatalysis of the water splitting. An average size of 40nm is present.

The size, structure, and composition of the resultant nanoparticles were characterized by TEM, XRD, it was shown that the bimetallic nanoparticles obtained were essentially monodispersed and that their mean diameters with a positive deviation were in the range of 20-50 nm. The bimetallic nanoparticles had a homogeneous alloy structure. The presence of carbon is clear which related to the electrode composition. Also traces of copper is noticed and this can be attributed to the wiring of electrodes [46].

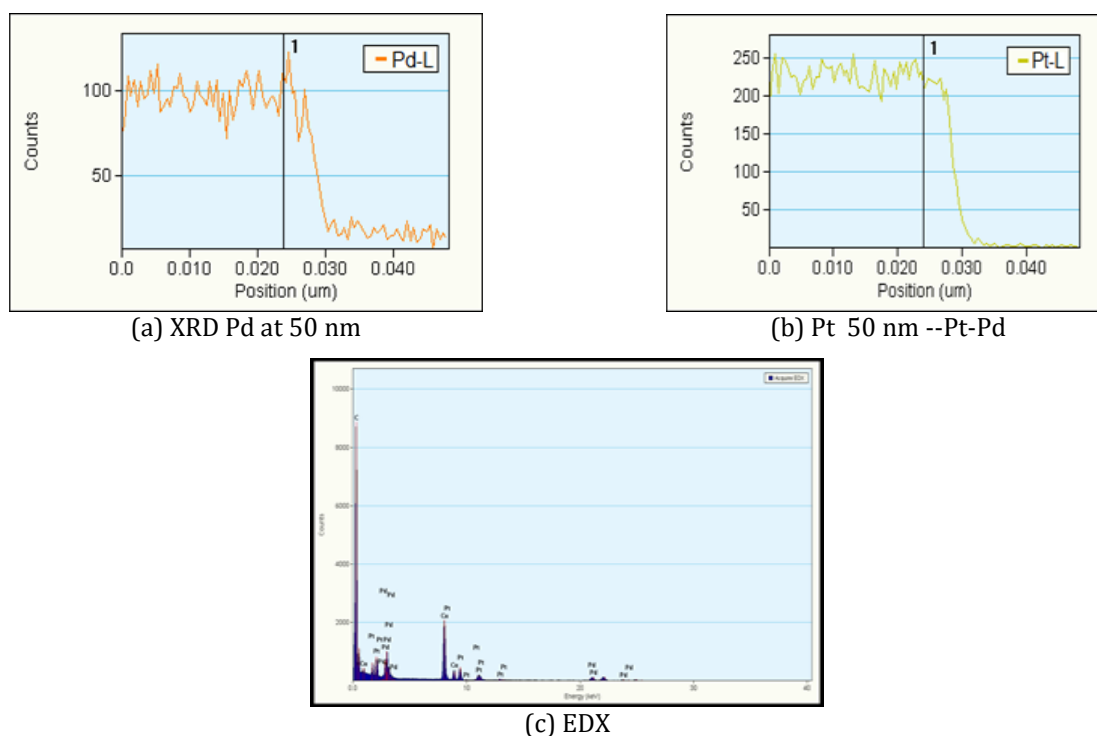


Fig. 7. Indicating XRD of Pt, Pd, and EDX of Pt, Pd

4. Conclusion and Future Perspectives

At the end it is found that when using the Pt-Pd catalyst the quantity of the energy was more than the Pt/C catalyst in the CV test. In the LSV test the reduction of the current was less in case of used the Pt-Pd that means our catalyst is better than the commercial one Pt/C. The development of better photocatalysts is also going to benefit from the recent progress in nano science, the electronic structure and the reactivity of nanostructures while synthetic methods can be employed for controlling the morphology of catalysts down to the nanoscale to further raise the efficiency of photochemical water splitting systems. Hydrogen productions have been considered as one of the most promising steps towards generating clean and renewable alternatives for fossil fuels. Recently, the shape- and size-controlled synthesis of noble-metal-based electrocatalysts for energy applications has attracted tremendous research interest. This is demonstrated by the increasing number of publications over the last decade concerning noble metal-based nanostructures of diverse sizes, shapes, and morphologies. While many of the previously published review papers focused on the recent developments in metal electrocatalysts.

Hydrogen represents a renewable energy alternative that may positively contribute to get over the global energy crisis while at the same time reducing its environmental burden. Overcoming the

challenge of reaching this potential could be helped by careful choice of hydrogen (H_2) sources. Photocatalytic generation of H_2 , although a minor alternative, appears to be a very good option at the time that liquid wastes are being degraded; therefore, this approach has given rise to an increasing number of interesting studies. Here, we aim to provide an integrated overview of the different photocatalytic, heterogeneous, homogeneous and hybrid systems. First, we categorize the units and mechanisms that take part in the photocatalytic process, and secondly, we analyze their role and draw comparative conclusions. Thus, we analyze the role of

- (i) the electron source to carry out proton reduction,
- (ii) the proton source, which can be free protons in the medium or a proton donor compound,
- (iii) the catalyst nature and concentration, and
- (iv) the photosensitizer nature and concentration.

We also provide an analysis of the influence of the solvent, especially in homogenous systems as well as the influence of pH. We provide a comparison of the photocatalytic performance, highlighting the advantages and disadvantages, of different systems. Thus, on the one hand, an update on the state of the art of photocatalytic generation of H_2 from a full perspective that integrates homogeneous, heterogeneous and hybrid systems, and, on the other, a source of useful information for future research.

Electrocatalytic water splitting driven by renewable energy input to produce clean H_2 has been widely viewed as a promising strategy of the future energy portfolio. Currently, the state-of-the-art electrocatalysts for water splitting in acidic solutions are IrO_2 or RuO_2 for the O_2 evolution reaction (O_{ER}) and Pt for the H_2 evolution reaction (H_{ER}). Realization of large-scale H_2 production from water splitting requires competent nonprecious electrocatalysts. Despite the advances of decades in this field, several challenges still exist and need to be overcome:

Most efforts in the design of non-precious electrocatalysts have focused on developing H_{ER} catalysts for acidic conditions but O_{ER} catalysts for alkaline conditions owing to their thermodynamic convenience, potentially, resulting in an incompatible integration of the two types of catalysts and thus inferior overall performance.

In conventional water electrolysis, H_{ER} and O_{ER} are strictly coupled and therefore H_2 and O_2 are produced simultaneously, which may lead to explosive H_2/O_2 mixing due to gas crossover. Meanwhile, the coexistence of H_2 , O_2 , and electrocatalysts could produce reactive oxygen species that might shorten the lifetime of an electrolyzer.

The H_{ER} rate is often limited by that of O_{ER} due to the more sluggish kinetics of the latter, which lowers the overall energy conversion efficiency. Moreover, the product of O_{ER} , O_2 , is not highly valuable. It remains challenging to develop efficient and low-cost H_2 storage and transport systems for the future. Hydrogen economy by catalytic water splitting to form hydrogen and oxygen has attracted considerable attention as a potential means of renewable energy production with no reliance on fossil fuels and no carbon dioxide emission. As illustrated in Figure 1, current successful photocatalytic systems for overall water splitting can be divided into two primary approaches. One approach is to split water into H_2 and O_2 using a single visible-light-responsive photocatalyst with a sufficient potential to achieve overall water splitting. In this system, the photocatalyst should have a suitable thermodynamic potential for water splitting, a sufficiently narrow band gap to harvest visible photons, and stability against photo corrosion. Because of these stringent requirements, the number of dependable, reproducible photocatalysts suitable for one-step water splitting is limited. The other approach is to apply a two-step excitation mechanism using two different photocatalysts. This was inspired by natural photosynthesis in green plants and is called the Z-scheme. The advantages of a Z-scheme water splitting system are that a wider range of visible light is available because a change in Gibbs free energy required to drive each photocatalyst can be reduced as compared to the one-step water splitting system and that the separation of evolved H_2 and O_2 is possible. It is also possible to use a semiconductor that has either a water reduction or oxidation potential for one side of the system. Example, some metal oxides (e.g., WO_3 and $BiVO_4$) function as a good O_2 evolution photocatalyst in a two-step water splitting system using a proper redox mediator, although they are unable to reduce water. Successful overall water splitting via two-step photoexcitation by visible light using several combinations of photocatalysts and electron relays has been reported. However, challenges remain in the promotion of electron transfer between

two semiconductors and in the suppression of backward reactions involving shuttle redox mediators. As we can expect from the reaction scheme shown in Figure 2, photocatalytic activity for overall water splitting is strongly dependent on the physicochemical properties of a loading nanoparticulate cocatalysts onto a photocatalyst significantly improves the water-splitting rate. Although some of the photocatalysts developed to date (e.g., layered compounds and tantalates) can decompose water without a cocatalyst, most require the loading of a suitable cocatalyst (such as NiO_x and RuO_2) to obtain a high activity and reasonable reaction rates. It is believed that the cocatalysts provide reaction sites and decrease the activation energy for gas evolution. Noble metals such as Pt and Rh are excellent promoters for H_2 evolution but can also catalyze a backward reaction, forming water from H_2 and O_2 , limiting their usefulness as cocatalysts for photocatalytic overall water.

Kinetic study on photocatalytic water splitting can provide us with rational strategies for improving the efficiency. During the development of photocatalytic systems for overall water splitting under visible light, a number of photocatalyst materials and preparation methods have been reported. Many studies have focused on the development of materials that are suitable for visible-light-driven overall water splitting by addressing light absorption properties, band edge position, crystallographic quality, particle morphology, and phase purity. However, it is difficult to understand what factor(s) dominates the net photocatalytic activity based on the above physical properties because the photocatalytic reactions proceed through a complicated sequence of competing multistep processes. This demonstrates the importance of understanding the kinetics and dynamics of a photocatalytic reaction to establish rational strategies for the immediate development of photocatalytic systems and for future practical applications. These results reflect a shortage of photoexcited carriers available for surface redox reactions under steady light irradiation. In summary, the experimental results indicate that the balance between the rates of redox reactions on the photocatalyst surface and carrier generation / recombination in the photocatalyst bulk determines the steady state charge concentration in the photocatalyst, that is, developing both a photocatalyst and a cocatalyst is important.

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