Medicinal Application of Palladium Nanoparticles

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Palladium (Pd), a noble metal, has unique properties for C-C bond formation in reactions such as the Suzuki and Heck reactions. Besides Pd-based complexes, Pd NPs have also attracted significant attention for applications such as fuel cells, hydrogen storage, and sensors for gases such as H_2 and non-enzymatic glucose, including catalysis. Additionally, Pd NPs are catalysts in environmental treatment to abstract organic and heavy-metal pollutants such as Cr (VI) by converting them to Cr(III). In terms of biological activity, Pd NPs were found to be active against *Staphylococcus aureus* and *Escherichia coli*, where 99.99% of bacteria were destroyed, while PVP-Pd NPs displayed anticancer activity against human breast cancer MCF7.

Keywords: palladium ; nanoparticles

1. Introduction

Recently, scientific research and industrial applications have been interested in transition metal nanoparticles (TMNPs) due to their unique optical, electronic, and catalytic properties [1][2][3][4][5][6][7][8][9]. Notably, noble metal NPs that include palladium (Pd) and ruthenium (Ru), rhenium (Re), rhodium (Rh), silver (Ag), osmium (Os), iridium (Ir), platinum (Pt), and gold (Au) have received a lot of attention in vast areas like sensors, energy conversion, biomedical treatment, and catalysis [10][11][12]. Palladium (Pd), which is the same group as platinum, possesses the unequalled electronic ground-state structure of Pd ($4d^{10}5s^{0}$) and the square-planar geometry of Pd(II) complexes with further axial positioned coordination sites, which can be expanded by employing numerous ligands, giving Pd distinctive properties for C-C bond formation and C-O bond cleavage [13].

Apart from this, palladium (Pd) NPs have received massive attention due to their exceptional properties that give them high catalytic activity and the ability to adsorb hydrogen at low temperatures. [14]. Additionally, they are also used in fuel cells, photothermal therapy, anticancer treatment, hydrogen storage, antibacterial applications, and sensors [15]. In addition, palladium NPs (Pd NPs) have been synthesized with high surface area and active sites [16].

In synthesizing Pd-based nanomaterials, one has to consider many points: (i) control of size and shape to reach an optimum of chemically active sites; (ii) control of high-index factors for enhanced catalytic activity; (iii) development of bi- and tri-metallic compositions and architectures to improve stability and activity; (iv) foundation of essential correlations between composition, structure, and reactivity of Pd nanomaterials to prepare highly competent catalysts; (v) finding new substrate materials with high chemical, conductivity, and mechanical stability, and also large surface area; and (vi) permitting the uniform distribution of Pd-based catalysts on support materials to enhance efficiency [17].

In this regard, Pd NPs were synthesized by three types of method: a chemical method [18], a physical method [19], and a biological method [20], but on the industrial scale, the physical method and chemical method were of interest. Physical methods included magnetron sputtering [21], physical vapor deposition [22], and laser ablation [23]. However, the synthesized physical method required expensive equipment and energy-intensive processes, including maintaining high pressure and high temperatures [24]. On the other hand, the chemical method depended on the chemical reduction of metal ions to zero-valent metal atoms and their nucleation to form NPs [25]. These methods include supercritical fluid nucleation [26], electrochemical deposition [27], sonochemical preparation [28], and wet chemical methods [29] such as the sol-gel method or reduction by alcohols or other reductants. The disadvantages of chemical synthesis methods involve reducing or stabilizing agents, hazardous solvents, or producing toxic side products [30]. However, biological methods, such as biogenic methods, are more interesting in pharmaceutical and biomedical applications due to the principle of providing simple, rapid, potentially more environmentally friendly, and cost-effective methods. Furthermore, the biogenic method has displayed control over physical properties of NPs such as size and shape [31]. Notably, the properties and performance of efficient catalysts depend on the shape and size of the nanomaterial; models for the shape-selective

synthesis of Pd nanostructures were published, such as Pd nanowires (Pd NWs), Pd broccolis (Pd NBRs), and Pd nanorods (Pd NRs) [32].

On the other hand, Pd NPs tend to agglomerate, leading to a decrease in the surface area. To overcome this problem, Pd NPs should be immobilized on the surface of a solid support such as metal oxide [33], silica [34], polystyrene [35], activated carbon [36], or carbon nanotubes [37]. A solid support helps to increase the activity of the catalyst by preventing the aggregation of Pd NPs, enhancing the stability and simplifying the recovery of the catalyst after the reaction, thus decreasing the cost and the chemicals used [38]. In addition, there are different ways to improve Pd NPs, such as bimetallic catalysts. Pd-based bimetallic catalysts, for instance, Pd-Cu, Pd-Ru, Pd-Ni, and Pd-Co, have shown high performance in catalytic activity and selectivity for goal products due to new properties of electronic and chemical structure [39].

2. Medicinal Application of Pd NPs

Researchers have discovered the effects of Pd NPs in photothermal, anticancer, and antibacterial applications. Thus, using Pd NPs improves wound-healing properties and antimicrobial, anticancer, and antioxidant properties (cf. **Table 1**). Unfortunately, there are not a lot of research studies about Pd NPs in the biomedical field. In general, metal nanoparticles are considered one of the most powerful antibacterial agents, and this strength comes from their thermal flexibility and their ability to act on multidrug-resistant microorganisms [40].

Table 1. Different Pd nanocatalysts reported for their biomedical application.

Catalyst	Application	Catalyst Loading	Temp	Time	Yield %	Ref.
microbial Pd-NPs	Kill *Staphylococcus aureus* and *Escherichia coli*	20 mg/L	37 °C	10 min	99.99	[41]
PdNPs/GDY	Destroy cancer cells	-	-	-	50	[42]
PdNPs/GDY combinate DOX	Destroy cancer cells	-	-	-	82.9	[42]
PVP-PdNPs	Breast cancer	10 µg/mL	37 °C	24 h	92	[43]

2.1. Pd NPs for Antibacterial Studies

Interestingly, antibacterial activity depends on the size and shape of Pd NPs. Some research illustrates that the larger size of Pd NPs has a lower effect in destroying *E. coli* than the smaller size. On the other hand, ultra-fine Pd NPs have vigorous activity in antimicrobial applications. In this regard, cubes and octahedrons of Pd nanocrystals are used to study the effect against Gram-negative and Gram-positive bacteria. Strikingly, the performance of Pd cubes with facets in destroying Gram-positive bacteria was more efficient compared with Pd octahedrons with facets; in contrast, the effect of Pd octahedrons with facets on Gram-negative bacteria was better efficient compared with Pd nanocubes [44].

The properties of Pd nanocrystals' oxidase and peroxidase activities have improved antibacterial activity's efficiency by producing reactive oxygen species (ROS). The way that Pd NPs damage microbes produces reactive oxygen species (ROS), causing harm to DNA and cell membranes and damage to proteins after destroying the electron transport system [45].

Some methods to kill bacteria depend on heat by converting near-infrared (NIR) light to heat, such as photothermal therapy (PTT), where PTT is an efficient and intact technique to transact with bacterial infections. Chen et al. used eco-friendly methods to prepare microbial Pd NPs by *Bacillus megatherium* Y-4. The cytotoxicity of microbial Pd NPs was investigated, where the result for microbial Pd NPs exhibited excellent biocompatibility. Also, it showed high antibacterial activity under NIR irradiation, where a low dose of Pd NPs (20 mg/L) was used to kill Staphylococcus aureus and Escherichia coli; during 10 min, 99.99% of bacteria were destroyed. Thus, Pd NPs can be used in PTT as an agent for fast sterilization applications due to Pd NPs having an efficient photothermal conversion ability [41].

In recent years, new methods have proven efficient in synthesizing nanoparticles with different shapes and sizes and have proven eco-friendly, such as the pulsed laser ablation in a liquid medium technique (PLAL). This technology inexpensively produces high-purity materials that depend on producing high-intensity pulses on a liquid material's surface [46]. Salman et al. successfully prepared Pd NPs using pulsed laser ablation with the liquid medium technique (PLAL). The study used Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacteria to investigate the effectiveness of

Pd NPs for antibacterial activity. Consequently, the performance of Pd NPs appeared to be more efficient in destroying Gram-negative bacteria than Gram-positive [47].

2.2. Pd NPs for Anticancer Studies

The unique properties of Pd NPs show them to be strong candidates for cancer treatment with the photothermal method because they have strong absorption in the NIR region, photostability, high photothermal conversion efficiency, biocompatibility, and different sizes and shapes depending on the synthesis route [48].

In this regard, many researchers have illustrated Pd NPs' mechanism for damaging cancer cells. According to literature reports, Pd NPs bond with nitrogen bases and phosphate groups of DNA and protein where the bonding is physicochemical, inhibiting their activity. Lactate dehydrogenase (LDH) is important for producing cellular energy; however, Pd NPs cause the leakage of LDH, thus having an effect on the activity of cancer cells. Moreover, Pd NPs produce free radicals of ROS and reactive nitrogen species (RNS), which damages the composition of lipids of cancer cells [49].

The leading cause of the quick proliferation of cancer cells is hypoxia, because hypoxia activates HIF-1 (a dimeric protein complex) that controls tumorigenesis and progression. In general, cancer cells produce a large concentration of H_2O_2. Therefore, the target of researchers is to raise the concentration of O_2 by decomposing the H_2O_2 produced by neoplastic cells, inhibiting the HIF-1 level and avoiding the pervasion of neoplastic cells. Liu et al. synthesized a two-dimensional (2D) nanocatalyst, including Pd NPs immobilizing on graphdiyne's surface (GDY). PdNPs/GDY play the role of oxygen generator by decomposing H_2O_2 into oxygen molecules inside cancer cells, thus preventing the rapid proliferation of neoplastic cells. The results proved that the efficiency of the antitumor effect was increased with the combination of PdNPs/GDY with a chemotherapeutic agent like doxorubicin (DOX) [42].

Breast cancer is a common cancer type in women, and it is regarded as curable in the premature stage of diagnosis. Ramalingam et al. successfully prepared PVP-PdNPs where polyvinylpyrrolidone (PVP) was immobilized on the surface of PdNPs utilizing an in situ single-step method. Moreover, the stability of PVP-PdNPs was proven due to the gain of Pd ions from pairs of electrons from the nitrogen or carbonyl oxygen of PVP. The performance of PVP-PdNPs was investigated by its anticancer activity against human breast cancer MCF7. Accordingly, PVP-PdNPs efficiently treated breast cancer MCF7 and had less cytotoxic activity against normal cells [43].

3. Energy-Related Applications of Pd NPs

Apart from the studies reported above, there are a plethora of reports with regards to the energy-related applications of Pd NPs such as fuel cells, solar cells, and hydrogen production and storage.

In a recent study, E. Mari et al. demonstrated the use of flower-like graphitic carbon nitride/iron oxide/palladium nanocomposite for the electro-catalytic oxidation of ethylene glycol as a useful technique for preparing fuel cells. The authors detailed the fabrication of a g-C_3N_4/Fe_2O_3/PdNPs/SPE nanocomposite-modified electrode by the electrochemical deposition method for ethylene glycol oxidation [50]. The proposed g-C_3N_4/Fe_2O_3/Pd NPs nanocomposite has exceptional electro-oxidation efficiency while being highly durable compared to commercial Pd/C and other recently reported electro-catalyst materials. Therefore, it is an competent electro-catalyst for direct alcohol-based fuel cell applications. The nanocomposite was found to be highly suitable for direct alcohol fuel cell applications, specifically for the electro-catalytic oxidation of ethylene glycol.

In another study, M.U. Rahman et al. developed an efficient and cost-effective counter electrode using 20 wt% of Pd NPs decorated on nitrogen-doped acetylene carbon black as dye-sensitized solar cells (DSSCs). The goal was to achieve higher power conversion efficiency and improve the overall performance of DSSCs. The outcomes showed that NCB@Pd displayed higher catalytic activity and efficiency compared to Pt, which was attributed to the nitrogen functional groups in the NCB support that modify the electronic structure of Pd, as well as the smaller particle size of Pd NPs with better dispersion, which provided improved electrolyte diffusability due to more active sites for redox reactions. Additionally, the support played a role.

Further work published by B.P. Vinayan et al. reported the synthesis of triangular-shaped Pd NP-decorated nitrogen-doped graphene, which was tested for its use as fuel cells and in hydrogen storage applications [51]. The study revealed that the as-prepared Pd/N-G exhibited higher hydrogen storage capacity compared to pure Pd nanoparticles, indicating the effectiveness of the spillover mechanism.

Another report by Kevin Dal Pont et al. [20] reported the preparation of Pd-based nanocomposites with a polyether block amide copolymer matrix while varying the percentage of Pd NPs. The nanocomposite with up to 20% Pd-based doping exhibited a typical response corresponding to ionic conductivity, with a decrease in σ' detected in the low-frequency spectral region. The pure polymer possessed conductivity of 5.1×10^{-9} S/cm; however, an increase in ionic conductivity was observed with an increase in doping of Pd NPs in the matrix [52].

Another research team, A.F. Oliveira et al., carried out some interesting work on the synthesis of palladium-doped titanium dioxide nanoparticles and their characterization for solar cell applications [53]. The reverse micelle sol-gel method was employed for synthesis of TiO_2 and TiO_2:Pd (i.e., doped with Pd), which yielded a satisfactory yield of between 80 and 90% for the synthesis of pure TiO_2 with various palladium dopings. The samples were subjected to impedance spectroscopy; from transmittance measurements employing Tauc plot fittings, the optical energy gap was established, which revealed that almost all the samples possessed good ionic conductivity.

4. Synthesis of Pd NPs

Lastly, the synthesis of Pd NPs is briefly mentioned. There are several approaches which include physical and chemical methods. The physical methods with which Pd NPs have been reportedly synthesized are magnetron sputtering [54][55] and laser ablation [56][57], while chemical methods comprise electrochemical deposition [58], sonochemical methods [59][60][61], and supercritical fluid nucleation [62][63][64]. Moreover, Pd NPS have also been extensively synthesized by biogenic methods such as the use of plant-based extracts as reducing/stabilizing agents for their preparation, i.e., *Pulicaria glutinosa* extract, *Origanum vulgare* L. extract, *Syzygium aromaticum* aqueous extracts, *Filicium decipiens* leaf extract, *Santalum album* leaf extract, dried leaf of *Anacardium occidentale*, etc., which yielded a variety of Pd NPs with varying sizes and shapes [65][66][67][68][69][70]. In addition to this, microbial-mediated synthesis using bacteria, fungi, algae, and yeast has also been successfully attempted [30][71][72][73][74].

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