Journal of Textiles, Coloration and Polymer Science
https://jtcps.journals.ekb.eg/

Egyptian Society for Textile Science and Technology
الجمعية المصرية لعلوم وتكنولوجيا النسيج

An overview on palladium nanoparticles and their usage in textile functionalization

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Abstract

Nanoparticles (NPs) are tiny materials with a size ranges from 1 to 100 nm, which have a unique physical and chemical properties due to their high surface area and nano scale size. Metal nanoparticles, especially those of the noble metals, are of wide interest not only because of their large surface areas but also because of their specific functions and potential applications. Palladium NPs is one of these noble metal nanoparticles. Palladium NPs can be biosynthesized as well as chemical synthesis. Textiles can be finished with metal nanoparticles such as palladium NPs which exhibit functional properties such as antimicrobial activity and ultraviolet (UV) protection.

Keywords: Metal nanoparticles, Palladium NPs, Antimicrobial activity, UV protection.

Introduction

Research on nanotechnology has been established since the turn of the century. [1-4] Materials of all kinds were manufactured at the Nano scale level via nanotechnology. A broad class of materials known as nanoparticles (NPs) includes particulate materials with at least one dimension of less than 100 nm. [5-19] These materials can have a 0D, 1D, 2D, or 3D overall form. When scientists discovered that a substance's size might affect its physiochemical properties, such as its optical qualities, they began to understand the significance of these materials. Twenty nanometer-sized particles of gold (Au), platinum (Pt), silver (Ag), and palladium (Pd) each displayed distinctive colors wine red, yellowish gray, black, and dark black, respectively as well as unique characteristics with size and shape variation that might be put to use in a variety of ways.

NPs are formed of three layers since they are not simple molecules. The first layer is the surface, which may be functionalized with a range of small molecules, metal ions, surfactants, and polymers. The second layer is the shell layer, which is entirely distinct chemically from the core; and the third layer is the core, which is the main part of the NP and is typically used to refer to the NP itself. NPs can be roughly classified into a number of types based on their size, shape, and chemical makeup. NPs are categorized into a few well-known types based on their physical and chemical properties. One of these kinds is metal nanoparticles (NPs), which are composed only of the precursors of metals. Metal nanoparticles (NPs) have superior features that make them useful in several fields of research. For the synthesis of NPs, a variety of techniques may be used, although they can be roughly categorized into two groups: (1) Top-down approach and (2) Bottom-up approach.[20] The Bottom-up method is used to synthesize nanoparticles (NPs) which are derived from bacteria, fungus, and plants. These NPs have a wide range of uses in science and technology. The amines, phenols, sugars, proteins, amino acids, aldehydes, and carboxylic acids found in microorganisms and plants are what cause the reduction of metal (II) to metal (0) NPs.

Palladium is one of the most active metals that works as a catalyst as it helps in reducing hydrogen and it is also effective in dehalogenation of waste water.[21, 22] Palladium is considered as a member of the platinum group metals which is known as an expensive noble metal. It has a unique catalytic activity owing to the fast hydrogen absorption into bulk palladium and its electron structure. Palladium belongs to group 10 in the periodic table (Pd $4d^{10}5s^{0}$). The totally empty fifth O-shell in palladium electron configuration is a unique phenomenon that takes its properties out of that of 10 group elements. It is the least dense and has the lowest melting point out of all the platinum group metals. Palladium dissolves slowly in concentrated

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Receive Date: 31 December 2023, Accept Date: 24 February 2024
DOI: 10.21608/jtcps.2024.259652.1309

nitric acid, in hot or concentrated sulfuric acid, and divides in hydrochloric acid.[23]

Biosynthesis of palladium NPs

The Bottom-up method is used to synthesize nanoparticles (NPs) which are derived from bacteria, fungus, and plants. These NPs have a wide range of uses in science and technology. The amines, phenols, sugars, proteins, amino acids, aldehydes, and carboxylic acids found in microorganisms and plants are what cause the reduction of metal (II) to metal (0) NPs.[21] In the past several decades, the biological sciences have paid a great attention to the production of metal nanoparticles, including gold, silver, zinc, platinum, palladium and others. Pd is receiving extra attention among other metal nanoparticles (NPs) due to its extensive usage as a catalyst in several organic transformations, such as oxidation and reduction processes. Traditionally, reducing and stabilizing chemicals are used to create Pd NPs by a variety of physical or chemical processes. However, in an effort to become green, there has been a paradigm change over time toward bio-inspired solutions for metal NP synthesis. These biological procedures have the advantage over traditional physical and wet-chemical methods due to their biocompatibility and ecologically friendly characteristics.[24]

Using Saccharomyces cerevisiae extract

Saccharomyces cerevisiae are a probiotic microorganisms, these organisms are surviving in low pH. The dry yeast of Saccharomyces cerevisiae is shown in the figure below.[21]

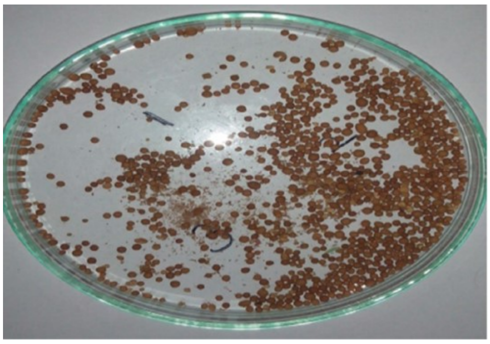

Fig. 1 Dry Saccharomyces cerevisiae

Synthesis of PdNPs [21]

1- 5 g of dry yeast granules was added to the 100 ml of water and stirred at room temperature for 30 min.
2- 10 ml of this aqueous solution was taken and added to 90 ml of palladium acetate solution with concentration of (1 mM), and the mixture was kept at room temperature for 24 h.
3- It will be noticed that color change from transparent to dark brownish color, which indicates the reduction of Pd(II) to Pd(0).
4- The PdNPs were separated by centrifugation at 5000 rpm for 15 min.

Using carboxymethyl cellulose

The most prevalent renewable polysaccharide on the planet is cellulose. Because it has carboxylate and hydroxyl groups, carboxymethyl cellulose (CMC) is a water-soluble polymer that is affordable, flexible, non-toxic, and biodegradable for use in a variety of scientific applications. It was documented the direct reduction of palladium species using CMCs as a green reductant, which resulted in the green synthesis of PdNPs supported by CMCs, which used CMC to create PdNPs as both a stabilizing and reducing agent because of the need to better understand the basic features of biopolymers and because of the current applications of green synthesis for PdNPs. So PdNPs would be physically encased in cellulose thin films, which might potentially be stabilized by the contact caused by cellulose hydroxyl group ligation. PdNPs-CMC Nano composites that were produced under control exhibited a number of characteristics, including strong catalytic activity and good stability.[22]

Synthesis of PdNPs [22]

1- A solution of $PdCl_2$ with concentration (10 mM), and a solution of CMC with concentration (1.0 wt %) were prepared.
2- The two solutions were added to a 10 mL flask, and a solution of NaOH with concentration (0.1 M) was added into the reaction mixture to adjust the solution pH at 6.
3- Then the mixture was heated at 80 ^{0}C controlled by water bath for 30 minutes forming PdNPs.
4- Changing the color, from pale yellow to dark brown depending on the PdCl2/ CMC ratio, indicates the forming PdNPs.

Using Lantana trifolia seeds extract

Fig. 2:

Preparation of Lantana trifolia seeds extract[25]

1- Lantana trifolia ripen blue black berries were first washed several times using distilled water then
2- 5 g of the plant were taken and sun-dried and then crushed into powder.
3- The resulting powdered was dispersed into flask containing 100 mL of distilled water, and the flask was stirred on a magnetic stirrer at 50 ◦C for 30 min.
4- The resulting extract was cooled down to room temperature followed by centrifugation at 6000 rpm for 5 min, then it was filtered through filter paper and stored at 4 ◦C.

Synthesis of PdNPs[25]

1- PdCl2 solution was prepared with 10 mM concentration.
2- 18 mL of the plant extract solution was added to 2 mL of PdCl2 solution in a beaker under continuous stirring for 2 h.
3- The reaction solution was treated with microwave irradiation for 2 min at 700 W power, then the color changed from orange to dark brown indicating the formation of PdNPs nanoparticle.
4- This dark brown solution was centrifuged at 2000 rpm for 30 min to separate the solid material, and the supernatant liquid was discarded.
5- The material was washed several times with ethanol, double distilled water, and finally dried at 80 ◦C for 2 h in an oven.

Chemical synthesis of palladium NPs

Although palladium's high material cost naturally limits its applicability, but a great deal of research has been done on Nano palladium. Palladium is a flexible catalyst that may be used in a variety of processes to generate carbon–carbon bonds, carbon–fluoride bonds, hydrogenation of alkynes to alkenes without further reduction into alkanes, and selective low oxide and alkanes oxidation. It works very well as an electro catalyst for the oxidation of primary alcohols in alkaline solutions when it is distributed over conductive substrates. Palladium undergoes extremely selective chemical changes when combined with a wide range of ligands.[23, 26, 27] Because of their high surface area, completely mono-dispersed metal nanoparticles are widely recognized to be excellent catalysts. At the close of the 20th century, a rapid growth of nanoparticle technologies began, despite the fact that chemists had previously ignored the realm of nanoparticles possibly due to its non-uniformity or polydispersity. It is now evident that metal–organic complexes, which consist of organic molecules and nano-metals with certain structures, may operate as a selective catalyst in a given process. Using polymers to stabilize and regulate the formation of noble metal nanoparticles is a common technique. Palladium nanoparticles (PdNPs) are stabilized by thiols, phosphines, phenantroline, and chiral diphosphite. These PdNPs may then be generated by reducing the appropriate metal salt that is encapsulated in different stabilizers. During the early stages of nucleation, the metal ion is reduced to a zerovalent metallic state, then metal atoms generate irreversible nuclei (size 0.1–1 nm) by additional collisions with other atoms or atomic clusters, which serve as seeds for the further generation of particles. In order to regulate particle Nano size and stop more agglomeration, protective agents must be added. Protective chemicals are classified according to their many stabilizing mechanisms, which include steric and electrostatic effects. While steric stabilization is achieved by the coordination of organic molecules (e.g., polymers, surfactants, long-chain alcohols) on the particle surface, electrostatic stabilization is based on the columbic repulsion force between individual nanoparticles, where ligands are adsorbed on the surface of clusters.[23, 28]

General View on Synthesis of Palladium NPs Using Wet Chemical Methods.

The chemical methods for NPs synthesis depend on the chemical reduction of metal ions to zero-valent metal atoms and their nucleation to form NPs. These methods include electrochemical deposition and wet chemical methods such as electrochemical deposition, sol-gel method, sonochemical preparation and reduction by alcohols or other reductants.[26, 27] The fundamental idea for wet chemistry's preparation of nano-particles is the reduction of the metal precursor with reducing agents with the presence of stabilizers provides protection. Special ligands or soluble polymers play an important part of the process since they have an influence effect on the stability, size, and shape of the final nano-partials. Ligands are nitrogen-containing organic compounds such as sodium sulfanilate and phenanthroline. The long chain of ligands increases the amount of the used stabilizer and lengthened the reaction time, which results forming in smaller PdNPs.[23]

Electrochemical deposition: In this method a direct electric current is Used, the metal cations are reduced and then deposited on the electrode of the electrolytic cell that is filled with a salt solution of the metal that wanted to be deposited. The positive metal cations are attracted to the surface of the electrolytic cell's cathode and reduced to zerovalent metal by obtaining the sufficient amount of electrons. The anode should be made of a substance resistant to electrochemical oxidation, such as lead or carbon, as in cases the reverse process (oxidation of the metal resulting in cations) may occur on the anode surface. For using this method, a chemical stabilizing agent such as poly (N-vinylpyrrolidone) (PVP) should be added into the solution to promote the formation process of Pd NPs, inhibit the electro deposition process of Pd onto the cathode, and stabilize the formed NPs.[26] Poly(N-vinyl-2-pyrrolidone) is widely utilized as a protective agent to produce ultrafine palladium nanoparticles. Because of the steric effect caused by the tail or loop segments of the polymers scattered in the solvent, this soluble polymer stops the preformed particles from coagulation.[23]

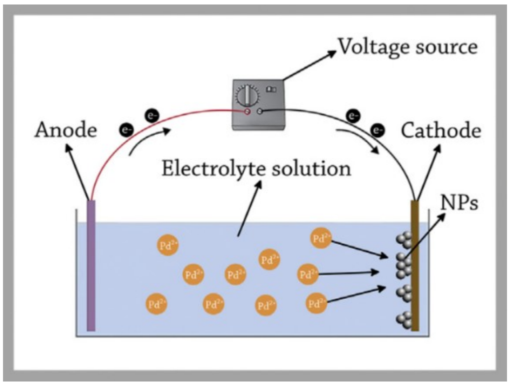

Fig. 3

Palladium NPs Synthesis Using Seed-Mediated Method.

In the last few years, there has been a lot of interest in the synthesis of noble metal nanoparticles using size- and shape-control techniques. Meanwhile, it has been documented that a number of synthetic methods, including hydrothermal, photochemical, seed-mediated growth, and thermal breakdown methods, are effective methods for producing noble metal nanoparticles (NPs) with specific sizes and shapes. The seed-mediated advanced method is becoming more and more common among these developed methods since it is one of the most efficient methods. Various noble metal nanoparticles (NPs) in the shapes of spheres, cubes, rods, plates, and even core/shell nanostructures have been successfully synthesized owing to the seed-mediated growth method's ability to operate at room temperature, in the presence of air and water. So for a wide range of upcoming applications, the development of novel synthetic techniques for generating Pd NPs with carefully regulated size and shape is important.[28]

Synthesis of PdNPs

1- Firstly a substrate of sputtered gold has been prepared from 99.99% pure Au source by thermal evaporation at a reduced pressure of 10-4 Pa., and has been used as a “seed colloid”.

2- 5 mL of H_2PdCl_4 solution (with concentration 2 mM) and 0.5 mL of 1% sodium citrate solution were added into a vial under magnetic stirring then 200 ml of H_2O_2 (30.62% w/v) was added.

3- After making sure of complete mixing, gold seed solution was added to the vial, and it will be noticed the change in color of the solution from yellow to gray.

4- Finally, the obtained suspension was centrifuged at different rotation speeds for 10 min, followed by rinsing.

palladium NPs in textile finishing

Studies were carried out to approve the importance of palladium NPs in doing the same role of the mordant in giving the dyed cotton fabrics an excellent color fastness with additional functions such as antimicrobial and UV-protection action, since showed the represented data that in absence of mordant, the pre-treated dyed samples exhibited excellent color strength, color fastness, antimicrobial action and UV-protection action.[24, 29-31]

Finishing Procedure: Cotton textile pieces were first treated with TA and Fe III in water to produce MPN-coated textiles, this coating occurred within 10 s and then the textile white color changed to purple. Then the MPN-coated pieces ware immersed in Pd (II) salt solution to form Pd NPs on the textile surface, producing brown-colored PdNPs-coated textile.[31]

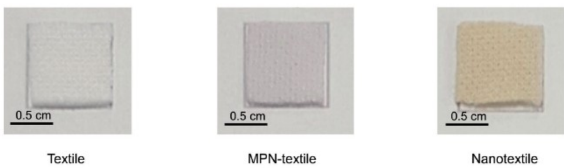

Fig. 4: TEM, SEM and EDX studies proved that the surface of the PdNPs-textiles was uniformly coated and that palladium NPs was well dispersed on the nano-textile surface.[31]

Antimicrobial Finishing Action

The antimicrobial action for the treated fabric was evaluated against S. aureus (G + ve bacteria), E. coli (G –ve bacteria) and Candida albicans through reduction percent and inhibition zone and it was estimated with excellent antimicrobial activities with (89.51%, 92.17% & 92.87%) respectively.[24, 29, 31]

UV-Protection Finishing Action

PdNPs treatment of cotton fabrics enhances the UV blocking properties. That is because the high light absorption of PdNPs in the UV region. This modification improves the UV blocking ability of the treated cotton and exhibits excellent UV protection ability strong UV protective ability. The UV protection categories of the treated cotton fabrics can be rated as good, very good and excellent, and the UPF values lie in the ranges between 40.2 and 64.4.[29, 30, 32, 33]

Conclusion

In the represented overview a study on palladium NPs is carried out to show the different ways of its synthesis even it was natural or synthetic way, and also to demonstrate the effective role of palladium NPs in textile finishing as it helps cotton fabric to gain antimicrobial activity and UV-protection.

Funds

The authors are grateful thank to the National Research Centre, Giza, Egypt for the financial support of this work

Conflict of Interest

The authors declared no competing interests in the publication of this article

Acknowledgment

The authors are gratefully grateful to acknowledge the Faculty of Applied Arts, Benha University. Furthermore, the authors are gratefully grateful to acknowledge the Central Labs Services (CLS) and Centre of Excellence for Innovative Textiles Technology (CEITT) in Textile Research and Technology Institute (TRTI), National Research Centre (NRC) for the facilities provided.

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نظرة عامة على جسيمات النانو بالاديوم واستخداماتها في الوظائف النسيجية

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المستخلص

جسيمات النانو هي مواد صغيرة يتراوح حجمها من 1 إلى 100 نانومتر، ولها خصائص فيزيائية وكيميائية فريدة بسبب مساحتها السطحية العالية وحجمها النانوي. تحظى جسيمات النانو المعدنية، وخاصة تلك الخاصة بالمعادن النبيلة، باهتمام واسع ليس فقط بسبب مساحاتها السطحية الكبيرة ولكن أيضًا بسبب وظائفها المحددة وتطبيقاتها المحتملة. جسيمات النانو بالاديوم هي واحدة من جسيمات النانو المعدنية النبيلة هذه. يمكن تصنيع جسيمات النانو المعدنية من البلاديوم بيولوجيًا وكذلك كيميائيًا. يمكن تشطيب المنسوجات بجسيمات نانوية معدنية مثل جسيمات النانو المعدنية من البلاديوم والتي تظهر خصائص وظيفية مثل النشاط المضاد للميكروبات والحماية من الأشعة فوق البنفسجية.

الكلمات الرئيسية: جسيمات النانو المعدنية، جسيمات النانو المعدنية من البلاديوم، النشاط المضاد للميكروبات، الحماية من الأشعة فوق البنفسجية.