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Synthesis and Application of Gold Nanoparticles in SPR Biosensors and Electrochemical Biosensors

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Abstract. Gold nanoparticles (AuNPs) have garnered high attention in the field of nanotechnology owing to their distinctive optical, electronic, and chemical properties. Therefore, AuNPs are particularly valuable in the development of advanced sensor technologies. It is well known that the size and structure of gold nanoparticles are significantly affected by the synthesis methods. Therefore, studying the preparation methods of AuNPs is of great significance for achieving controllable performance. This would promote the application of AuNPs in biosensor. This paper discusses the synthesis methods of AuNPs, including the Turkevich, Brust-Schiffrin, seeding growth, and green synthesis techniques. In addition, the affection of the synthesis method on the morphology and functional properties of AuNPs are analyzed critically. The paper also explores the applications of AuNPs in biosensors, especially in surface plasmon resonance (SPR) biosensors and electrochemical biosensors. The modification of the sensors by AuNPs is proved to significantly enhance the sensitivity and specificity. This work contributes to achieve accurate and efficient detection of biological molecules.

Keywords: Gold nanoparticles; Biosensor; Synthesis; Application.

1. Introduction

Gold nanoparticles (AuNPs) are smaller particles of gold within the nanometer range. It was first reported at 1857, by Michel Faraday. It was found that the AuNPs absorb light at 450 nm while AuNPs reflect red light of 700 nm [1]. After that, due to the distinctive optical, electronic, and chemical properties, AuNPs are highly valued by researchers [2]. In the past several years, AuNPs have been applied in a variety of fields, such as biomedicine and biosensors. Biosensors are devices which are sensitive to biological substances. They can convert their concentrations into electrical signals for detection. It is reported that the AuNPs can influence the performance of the biosensor due to their unique property. According to previous reports, AuNPs can help improve the sensitivity of biosensors. It can also effect the electric property in electric biosensor. Therefore, biosensors based on AuNPs have become excellent candidates in this field.

The different synthesis methods affect the structure and properties of AuNPs. Therefore, studying the synthesis methods of AuNPs is of great significance for exploring AuNPs based biosensors. The AuNPs can be synthesized in various ways. The size of the AuNPs will effect the property of the sensor. Therefore, exploring the synthesis methods which can prepare AuNPs with controllable structures becomes a research hotspot.

In this paper, the synthesis of AuNPs is discussed in detail. Besides, the applications of AuNPs in biosensors are also outlined.

2. Synthesis of Gold Nanoparticles

The synthesis of gold AuNPs has been a focal point of nanomaterials research for several decades. Diverse methods have been developed to optimize the diameter, shape, or functional properties of AuNPs. Among these, the Turkevich method, Brust-Schiffrin method, and seeding growth techniques have been particularly influential.

2.1. Turkevich Method

This method can synthesize AuNPs which have diameter of about 20 nm. It depends on the reduction of tetrachloroauric acid. The first step of this method is boiling a solution of tetrachloroauric acid. Then trisodium citrate dihydrate is added quickly with stirring. After several minutes, the AuNPs will form. This method is straightforward and easy to use. The distribution of AuNPs mainly effected by the three factors. The pH of the mixture which in reaction has a significant impact on the formation of products. Besides, changing the concentration of reactant and the ionic strength will also have an impact on the product. These factors have relationship to the distribution of hydroxy-chloroauric species, zeta potential, and screening strength [2].

Furthermore, in the past few years, some researchers have developed methods based on this one. For example, in the research by Sankar et al., they found that inverting the order of the solution addition can induce the formation of AuNPs with smaller sizes and narrower distribution. Depending on this improved method, AuNPs with a diameter of about 5.2 ± 0.7 nm can be obtained [3].

2.2. Brust-Schiffrin Method

Brust et al. proposed this method which is based on a two-phase liquid-liquid system. AuNPs form when tetrachlorocuprate ions are reduced with sodium borohydride in the presence of dodecanethiol. In this method, the diameter of the AuNPs is about 1-3 nm. Interestingly, the AuNPs which formed in this method display some unique properties. The as-prepared AuNPs can be handled and characterized as a simple chemical compound [2]. During the reaction, the thiol molecules self-assemble on the surface of the growing gold nuclei. In addition, XPS analysis indicates that the gold primarily exists in the Au (0) state with cuboctahedra.

2.3. Seeding Growth Method

The seeding growth method is an effective method which is used to prepare AuNPs. The advantage of this method is rapid, economical, and highly controllable. It uses gold particles with diameter of 3.5 ± 0.7 nm as seeds. The ration between metal salt and seed particles can control the diameter of AuNPs within the range from 5 nm to 40 nm [4].

Jana et al. used various ratios of seed solution and metal salt solution to prepare AuNPs with different sizes [4]. By increasing the seeds, a mean diameter of 5.5 ± 0.6 nm can be obtained. However, a particle diameter of 8.0 ± 0.8 nm can be observed when the number of seeds are reduced. Afterwards, metal salt are added at a slow rate until eventually the nanoparticles with an average diameter around 37 ± 5 nm are synthesized.

The data presented by Jana et al. also indicates that the size distribution of particles changes as the particle diameter increases. For instance, the size distribution standard deviations for particles with diameter of 5.5 nm is 11%. While that of the AuNPs with diameter of 8.0 nm is 10%. However, when the diameter increased to 17 nm, the standard deviation rose to 15%. This change in size distribution is associated with the diversity of particle morphologies. It is reported that small number of rod-shaped particles were observed alongside the spherical particles in the 37 nm sample. Besides, adjustable shapes are considered as the major advantage of the seeding growth method [4].

2.4. Green Synthesis

Green synthesis primarily utilizes has three biological materials, bacteria, fungi, and plant extracts. It often incorporates auxiliary techniques such as photochemistry, ultrasound, and microwave methods. These approaches offer environmental benefits and avoid harmful chemicals, making them highly promising for biomedicine and environmental sciences [3].

The shape and size of nanoparticles can be changed by adjusting factors such as pH, temperature, and reaction time. These adjustments occur during green synthesis process. Vijayaram et al. mention that pH and temperature can influence the shape and size of nanoparticles. It is also reported that reaction time is critical in determining final morphology [5]. For instance, extending the reaction time typically results in larger nanoparticle sizes, affecting their performance in various applications. These adjustments provide greater flexibility and adaptability in meeting specific application requirements [6].

3. AuNPs in SPR Biosensors

Surface plasmon resonance (SPR) is a powerful technique used to detect molecular interactions in real-time without labels. This relies on the excitation of surface plasmons occurring at the interface between a metal. This interaction induces electron collisions, affecting the reflection angle, which can be detected.

AuNPs are important candidates in enhancing the SPR signal due to their unique properties. The interaction of light with AuNPs cause a localized surface plasmon resonance, which enhances the electromagnetic field near the nanoparticle surface. This enhancement significantly increases the sensitivity of SPR-based sensors. Huimin et al. discovered in their research published in 2023. They use 1, 6-hexanedithiol (HDT) to prepare AuNPs directly modified gold film. They found that using gold film which is functioned by AuNPs can help to excite LSPR. It decreases the penetration depth by approximately 28-fold and amplifies the surface electric field intensity by around 4.6-fold. This enhancement results in a sevenfold increment in the carcinoembryonic antigen immunoassay, demonstrating that AuNPs can significantly enhance the performance of the biosensors [6].

AuNPs can increase the sensitivity of SPR sensors. They can amplify the SPR signal and enable the detection of low-concentration analytes. The mechanism of the enhancement of signal can be summarize as two points. The initial factor involves the electronic coupling between the localized surface plasmon of AuNPs and the propagating plasmon on the SPR gold surface. The second factor pertains to the high density and molecular weight, which result in an increased apparent mass of the analytes immobilized on these nanoparticles. Additionally, AuNPs are highly versatile and can be functionalized with various biomolecules, allowing for the detection of a wide range of targets. Furthermore, the AuNPs-based SPR biosensors can be made into an array format. It can offer expeditious and high-throughput screen biomolecular interactions. In 2000, a demonstration of this in a biosensor of this type was provided by Okamoto and colleagues [7].

In conclusion, gold nanoparticles play a significant role in enhancing the performance of SPR sensors. Their unique properties and the ability to be synthesized in various ways make them invaluable in numerous applications, particularly in the field of biosensing.

4. AuNPs in Electrochemical Biosensors

This type of biosensors can translate biological events into electrical signals. They have attracted much interest over the past decade due to their easy and economic detection capabilities. A typical challenge in electrochemical biosensing is the electron transfer between redox proteins and the electrode surface. Most oxidoreductases have thick insulating protein shells around their active centers. Electrochemical biosensing experiences diminished analytical performance in the absence of electron transfer mediators, as the electron transfer between electrodes and active centers is impeded. However, AuNPs can act as wires to enhance electron transfer [2].

This property has been proven by Natan’s group. Their experiments show that when nanoparticles aggregated, the electrochemical behavior became irreversible or only quasi-reversible. This phenomenon may be due to the aggregated nanoparticles providing sites for irreversible protein adsorption, thereby weakening the electrochemical signal. In contrast, well-dispersed 12 nm diameter gold nanoparticles demonstrated the best electrochemical performance, while smaller or larger nanoparticles, as well as aggregated particles, performed less effectively. This suggests that the aggregation state of the nanoparticles affects the surface area. Meanwhile, they are proved to have a profound impact on the electrochemical reaction processes of the protein.

Furthermore, AuNPs play a role as the stationary platform for biosensor. Gold nanoparticles are an ideal substance for use as a platform due to their ability to absorb biomolecules while maintaining bioactivity and stability. This is primarily attributed to their high biocompatibility and surface free energy. AuNPs display high surface areas, which can increase the number of protein-binding sites.

5. Conclusion

AuNPs have become a cornerstone in the development of nanomaterials, largely due to their distinctive physical and chemical characteristics. This paper begins by discussing the synthesis methods of AuNPs, focusing on how different techniques. The Turkevich, Brust-Schiffrin, seeding growth, and green synthesis methods are highlighted. Affecting factors which determine the size, shape, diameter, and surface properties of the nanoparticles are discussed. These methods are critical as they could determine the functional characteristics of AuNPs, which in turn influence their application in various sensor technologies.

In particular, the paper delves into the role of AuNPs in enhancing the performance of biosensors. The application of AuNPs in SPR sensors is highlighted, demonstrating how the localized surface plasmon resonance effect of AuNPs amplifies the SPR signal. The sensitivity is reported to be enhanced and the detection of low-concentration analytes can be achieved by this method. The versatility of AuNPs is further explored in the context of electrochemical biosensors, where they facilitate electron transfer and improve the overall performance of the sensors.

The integration of AuNPs into these sensing platforms improves their sensitivity and selectivity. Moreover, opens new avenues for the development of high-throughput, cost-effective, and accurate biosensing technologies. This review underscores the importance of AuNPs in advancing sensor technology and suggests future directions for research in this rapidly evolving field.

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