Detection of Heavy Metal Ions Based on Gold Nanoparticles

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Abstract. Gold nanoparticles, abbreviated as AuNPs, have been widely used in catalysis, optics, electronics, and biotechnology due to their unique performance brought by large specific surface area. In recent years, with the improvement of health awareness, the use of gold nanoparticles to detect heavy metal ions has become a research hotspot. The detection is based on colorimetric techniques, which means the metal ions are detected through the color change in solutions. This color change is visible or could be distinguished by ultraviolet-vissible spectrometers. Numerous studies have been published on gold nanoparticles, especially for its synthesis methods. This work introduced the chemical, physical, and biological preparation methods of gold nanoparticles. Understanding mechanisms for detecting heavy metal ions using AuNPs is also very important. Aggregating mechanism, anti-aggregation mechanism, and etching mechanism were also introduced. In addition, applications of using AuNPs to detect heavy metal ions were also introduced. This work will help promote the further development of this technology.

Keywords: AuNPs; heavy metal ions; detection method.

1. Introduction

Heavy metal ions exist in industrial pollutants and may enter human bodies through natural food chain, bio-concentration or even direct contact. Heavy metal ions that have already entered the human body can cause varying degrees of damage to the body. For example, when the mercury ions in human bodies accumulate to a certain concentration, poisoning symptoms would take place. The nerve system will be seriously hurt, causing swirling and headaches, while organswill be badly injured. Mercury pollution mainly comes from human activities, including istewater that emitted by battery, electric and plastic industries and lack of dumped medical instruments. Lead is another toxic heavy metal element. The symptoms of lead poisoning include developmental delay, abdominal pain and fatigue in children. For the newborns, lead poisoning causes low birth weight and prematurely born. Adults who are influenced by lead in their body would show the symptoms such as difficulties in memory and concentration. Copper is also a trace element necessary for life. People intake copper through food and water, where copper exists in the state of copper (II) ions. Copper pollution in natural water comes from the waste emission from industrial manufacturing, metal smelting and electroplate factories. The basic clinic symptoms of copper poisoning are epigastric pain, nausea, vomiting, and diarrhea [1].

With the continuous improvement of health awareness, an efficient technique to detect those ions in natural water is becoming increasingly important. Many detection methods for heavy metal ions have been established by researchers. Among them, sensors based on gold nanoparticles exhibit excellent performance in detecting heavy metal ions. Gold nanoparticle sensors have the advantages of diversity and high detection efficiency. The key material to achieve such excellent performance is gold nanoparticles. Therefore, it is of great significance to study the basic properties, preparation methods, and detection mechanisms of gold nanoparticles.

2. Material and Properties

Gold is one of the most stable elements. However, gold particles on the nanometre scale have its unique photo-electricity, physical chemistry properties and excellent bio-compatibility. This brings gold nanoparticles wide variety of applications, for instance, building biosensors.

AuNPs is a good conductor of electricity so it can be used to improve and enhance the electrodes in biosensors. Another property of AuNPs is Surface Plasmon Resonance (SPR). There are free located upon AuNPs. The SPR effect will come into being while a specific formant appears within the Uv-Vis area. This takes place as an incident ray stimulates the free electrons. Gold nanooparticles are also efficient catalysts. In 1989 scientists reported that materials such as iron (II) oxide and titanium (IV) oxide carrying AuNPs with high dispersibility have excellent catalytic activities on many reactions [2, 3]. Due to its optical properties, gold nanoparticles are used in an electrochemical sensor that showed high stability, accuracy and sensitivity in recent studies. AuNPs also has excellent biocompatibility, and the biosensor consists of gold nanoparticles and carbon materials (graphene and carbon nano tube) showed high sensitivity in biological applications [4].

3. Production Methods

The basic principle of the chemical method is dissolving and adding reducing agent when stirring the solution. The reducing agent reduces ions in the solution into neutral gold ions. For example, the Brust-Schiffrin method is based on reducing Au^{3+} using $NaBH_4$ stabilized by thiols. This technique shows evident features that AuNPs produced are able to have narrow distribution and controllable sizes [5].

The feature of the Brust method is that the diameter and distributions of the particles can be controlled and the thiol functionalizes the surface of the particles.

However, chemical synthesis has several disadvantages that mainly come from using very harmful chemicals and causing environmental pollution. In addition, the carcinogenic solvents involved restrict the use of the AuNPs produced in the clinical field. Physical techniques used to produce gold nanoparticles involves using γ -rays, UV radiation, ultrasonic waves or lasers. This causes an evident error that the production process requires expensive equipment, large amount of energy consumption and various steps of product purification. This means that the cost of making AuNPs is high. The biological synthesis of AuNPs works as an efficient tactic. This is because it has advantages in important aspects such as cheap process, safe materials, less reagents required, size-controlled products, clean resources and high efficiency [6, 7]. In a recent study, streptomyces flavolimosus is used as a biological method for AuNPs synthesis. The $HAuCl_4$ and cell-free supernatant solutions are mixed at the volume ratio of 1:2. The mixture is stored under constant temperature without illumination for days. The red/dark purple color of the mixture showed the presence of AuNPs produced [8].

4. Mechanism for Detecting Heavy Metal Ions Using AuNPs

Recent years with the widely use of AuNPs on detecting heavy metal ions, the system of colorimetry detection has been systematically researched. The theoretical basis of the detection systems is similar. Differences in aggregation status of AuNPs would lead the change of SPR absorption peak which would result in the change of the color. This is used to realize the naked-eye colorimetry half-quantitative determination. Quantitative determination can also be achieved by using UV-Vis. Understanding principles for detecting those harmful ions using AuNPs is crucial for further utilizing it.

4.1. Aggregating Mechanism

In the late 20th and the early 21st century, using DNAzyme to embellish the surface of AuNPs, the detection of ions through aggregating and anti-aggregating approaches was realized.

For the aggregation mechanism, the surface modification of gold nanoparticles is done during or after the synthesis. This leads to the result that the specific functionalized reagent is adsorbed to the surface of nanoparticles. The detected heavy metal ions will be complexed with specific reagents on the surface of nanoparticles. That is, the complexation reaction between cations and ligand anions or

molecules is the basic principle, resulting in the aggregation of monodisperse nanoparticles. This causes the SPR absorption peak of functional gold nanoparticles to red-shift or with the widening of peak type and the decrease of absorbance, and the corresponding color change of the sol.

4.2. Anti-aggregation Mechanism

The anti-aggregation mechanism is the opposite of the aggregation mechanism. The synthesized gold nanoparticles are functionalized and coated with a layer of specific functionalized molecular substances. The addition of certain compounds can lead to the aggregation of functional nanoparticles. When the compound is added to the functional nanoparticles at the same time as the target detected heavy metal ions, the aggregation reaction of nanoparticles will not occur again. As a result, it is called the anti-aggregation mechanism. This detection mechanism has been widely used in detection.

4.3. Etching Mechanism

The etching mechanism has redox reaction as its theoretical foundation and is mainly used on the detection of heavy metal ions with redox quality (e. g. Cu^{2+}). Through pH adjustment of gold nanosol and other conditions optimization, specific redox heavy metal ions can react with zero valence gold on the cover of AuNPs. The size of AuNPs gradually gets smaller, causing the blue shift of SPR absorption peak and the change of light absorption intensity. At the same time, the sol color will also change accordingly.

5. Applications

The study on Hg^{2+} is the most common since the mercury ions are the most toxic. Scientists like Zhang developed a technique based on the mechanism of core-shell mode in the field. The process is taking precipitation reaction as the basic reaction principle, thioacetamide is hydrolyzed under acidic conditions to produce H_2S, which is adsorbed to the AuNPs surface [9]. It reacts with on the AuNPs surface to produce precipitation and deposition on the AuNPs surface, resulting in changing the surface state of gold nanoparticles. The SPR absorption peak then changes, and blue shift occurs. The former color shown by the gold sol was wine red. Detection was achieved when it turned blue.

Another group of research like Ghann use an improved Frens method. The gold nanoparticles are prepared by mixing gold salt with trisodium citrate dihydrate solution while stirring for a quarter. A series of color changes showed the production of AuNPs. The color of the mixture has obvious differences. The research team uses a colorimetric method to determine Pb^{2+}ions. Through the exchange reaction between the AuNPs produced by the citrate method and the ligand. The lipoic acid acts as the ligand and is disulfide group reacts with the gold nanoparticls at one end for attachment and reacts with the lead ions at the other end of carboxylic acid. The gathering caused by interacting with leads to color changes from ruby red into purple [10].

Another research detects heavy metal ions in a new way. Concentration of valine solution used in the experiment is 0. 1M and is stored in MilliQ water. Diluted NaOH solution is added to adjust the pH. The solution is then boiled when stirring before is added so that the concentration of the gold salt is 1mM. The boiling process is sustained with continuous stirring till the color changes from light yellow to dark purple. The solution is then cooled and divided into equal samples. For the metal ions determination, the gold nanoparticles synthesized is disposed with metal solutions in the ratio of 1:2 and the optical properties are recorded after constant time intervals. The sensitivity of AuNPs in a range of concentration is also studied in the experiment. UV-Vis spectrometer and DLS are used to analyse the disposed solution. In addition, metal interference in studied by treating AuNPs with 100ppm of solution and 100ppm of other metal ions (such as Cu^{2+}, Ba^{2+}, Hg^{2+}, Cr^{3+}) separately.

Another sensitive and selective approach for lead ions detection is done by Zhong [11]. The gold nanoparticles are prepared with the Frens synthesis. The basic principle for the detection is supervising the behavior of AuNPs when GSH exists in the surroundings. GSH is a non-protein tripeptide. The existence of GSH causes the gathering of AuNPs. The standardization of AuNPs size

acts a significant role for realizing excellent optical properties so that the sensitivity and selectivity can be high for the detection method. The -SH group are attracted by the gold. When GSH exists in gold nanoparticle suspension, Au-S covalent bonds are expected to form. At the same time, hydrogen bonds are formed between GSH molecules even if they are absorbed to the surface of AuNPs. This property enables GSH molecules to aggregate AuNPs under specific conditions. Lead ion (Pb^{2+}) is able to motivate the gathering of GSH-modified gold nanoparticles under specific pH measures through forming coordination complexes with carboxyl group (-COO-). Color of the gold nanoparticle solution was ruby red originally. After a short period, it turned into blue.

6. Conclusion

The development of new materials has promoted progress in the field of technology. AuNPs exhibit excellent electrical and optical properties. Based on the unique performance of AuNPs, they can be used to detect heavy metal ions. Colorimetric method based on AuNPs is an efficient technique for determining heavy metal ions. In this work, various common preparation methods for AuNPs were introduced. The mechanism of using AuNPs to detect heavy metal ions has also been discussed in detail. In summary, this detection of heavy metal ions is very effective. Further expanding the application scope of this technology in the future will be the direction of future development.

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