Heavy Metal Ions Detection in Cosmetics: Nanogold Based Sensors

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Abstract. Makeup has become an important way for people to pursue beauty. At the same time, heavy metal pollution in cosmetics is receiving increasing attention. In order to improve the quality of cosmetics and promote the development of cosmetics industry, finding a convenient and obvious method to detect heavy metals ions in cosmetics has great significance. Large numbers of detection methods have been established, among which the most noteworthy is the detection method based on nanogold sensors. Nanogold is a new type of material with unique properties at the nanoscale. Therefore, sensors based on nanogold are highly promising for detecting heavy metal ions in cosmetics. Especially in recent years, as people pay more and more attention to health, the number of related studies increased significantly. Therefore, it is very important to learn about the heavy metal ions using nano gold sensors. In this work, the search for bad ions of metal on nanogold sensors has become the research object. The nanogold sensor's detection technique was described and contrasted with other processes. Consequently, nanogold sensors for the detection in cosmetics will improve further.

Keywords: Nanogold sensor, cosmetics, heavy metal ions.

1. Introduction

Makeup is an effective way for people to improve their appearance. From ancient times to the present, people are eager to look attractive. In order to pursue beauty, many people choose to makeup They use various types of cosmetics, such as eye shadow, blush and lipstick [1]. However, some manufacturers add heavy metal ions to ensure the efficacy of cosmetics. For example, the detection rate of lead in some non-standard foundation make-up is high [1]. When these metal ions are excessive, they can cause great harm to the human body. These harmful ions can adsorb on the surface of the skin. They can enter the blood, and then enter the organs. Finally, they accumulate in the human body. It may cause allergic contact dermatitis or even worse [2]. In order to basically eliminate this hazard, many countries have issued relevant laws and regulations to regulate the content of heavy metals in cosmetics. The earlier techniques include induced coupled plasma mass spectrometry and electrochemical deposition technology [2]. This analysis methods-based instrument still has some drawbacks. Therefore, it is necessary to explore more sensitive electrochemical sensors. It can determine the content of unpleasant ions. Recently the test for toxic ions in makeups has become a hotspot, so it is urgent to summarize the research results in this field. Therefore, this study will concentrate on the harmful metal ion and how they are found. AuNPs is a kind of nano gold inorganic particles with size of 1~100nm. AuNPs usually display good biocompatibility. Since the Middle Ages, AuNPs have been widely used in biochemistry and drinking gold. At that time, it seemed to have a good therapeutic effect on various diseases. However, there were large numbers of side effects due to the lack of understanding of gold nanoparticles [2]. Modern nanotechnology has led to the invention of sensors based on nanoparticles, which have drawn a lot of attention.

This paper will discuss its role why and how the bad ions are detected in cosmetics. Firstly, the working principle of electrochemical sensor based on gold nanomaterials was introduced. In addition, the law is based on existing literature and figures were concluded. Understanding the detection principle helps to better utilize this detection method. This work also summarizes other analytical characterization methods.

2. The synthesis of AuNPs

As a matter of fact .at start, the AuNPs were synthetized from HAuCl along with citric acid in boiling water. The citriate played the roles of both reducing agent and stabilizing agent. This process was mostly used in manufacturing diluted spherical AuNPs solution at around 10~20 nm [4]. AuNPs will firstly experience a two-phase synthesis by reduction of $HAuCl_4$, in the presence of alkanethiols as the stablizing agent.

In 1994, an innovation was fulfilled in GNPs synethesis by chemists Brust and Schriffin. They created stabilized nanogold particles in alkaline through a biphasic reduction by inputing tetraethylammonium bromide (TOAB) as the reagent that converting phase and sodium borohydride as the reducing agent [5, 10].

There are also another two methods of preparation mothod, crystal seeding method and the green sythesis method [5]. For the con of first method, it is relatively hard to find a suitable condition for tne seed to grow. There are also a lot of factors that may affect the making process such as the seeds' concentration, the reducing agent and the amount of reducing agent added. Sometimes the by-products may also contaminate the environment. As for the green synthesis method, it is environmentally friendly, but it is also very time-consuming. Biased AuNPs might form if it is lack of mechanical blender inside body of organisms, and this green method is also very energy consuming.

2.1. How nanogold particles detect heavy metal ions

Nanogold is the key material of this kind of sensor. It is very important to understand its preparation and mechanism. AuNPs not only have the specific surface effect and quantum size effect of general nanoparticles, but also have good biocompatibility and unique optical properties. AuNPs solution is usually pink. Its colour will turn to blue or purple after combining with the target object. When the frequency of photons emitted into the metal is the same as the frequency inside the metal, the electrons connected to conduction on the gold nanoparticles' boundaries resonate under the action in outer side, known as surface plasmon resonance (SPR). This macroscopic performance is the selective absorption of the incident light by nano particles of Au. With the zenith abosrbed of SPR appearing at one or more wavelengths, AuNPs are very sensitive to the environment. When the shape, size, nanoparticles' distribution and the dielectric constant of the surrounding environment varies, the distribution of gold nanoparticles will also change. Thus, leading to the variation of SPR spectrum. When gold nanoparticles gather or disperse, the absorption peak red shift or blue shift. The colour of solution will also change. This lays the foundation for the realization of visual determination of harmful particles.

In fact, the detection of heavy metal ions by SPR effect of AuNPs can be divided into two modes: nonfunctional mode and functional mode. According to the different recognition molecules, functional molecules can be divided into amino acids, peptides, proteins, aptamers, nucleases, etc. [8]. These functional molecules are divided into biological molecules and abiotic molecules [8]. Biological molecules such as amino acids, peptides, proteins, aptamers, etc. form S-Au on the surface of AuNPs through electrostatic and hydrophobic interactions, forming functional AuNPs. The increase in noxious ions is actually guiding the aggregation and depolymerization of functional AuNPs, so as to realize the gauging of detrimental metal ions in maquillage.

The nonfunctional AuNPs obtained by sodium citrate reduction method can also be used for the detection of heavy metal ions in cosmetics [5]. A layer of negatively charged silver citrate was coated on the exterior side of nonfunctional AuNPs prepared by sodium citrate method. By adding o-phenylenediamine, nonfunctional AuNP aggregates and the solution will alter [7]. After detecting divalent copper ions, silver ions or mercury ions, metal ions will continue to reduce to form small nano mercury, nano copper and nano silver. The rate of reactions of $Hg^{2+,}$ Cu^{2+} and Ag^{+} will be increased with o-phenylenediamine [6]. As the concentation of o-phenylenediamine decreased, AuNPs depolymerized and the colour of solution varies. The detection results of the three ions were quite different. It may be due to their different oxidation ability. The colorimetric method can

eliminate the interference of the other two ions by adding one or two suitable masking agents. The reliability of the method is proved by the indication of them in water of pound. [5]

2.2. Hazards

In order to ensure the function of cosmetics, a lot of manufacturers choose to add heavy metal ions into the makeups and reduce the prime cost simultaneously. Whitening and concealing cosmetics are often having mercury ions inside, which may leave injuries to human body. It also has a significant impact on the developing brain and nerves of fetuses for fetuses. Moreover, it even affects the cognitive thinking, memory, and language abilities after they are born. The environment is very important in the production of cosmetics. Cosmetics produced in improper environment may also exceed the standard of heavy metals. The focus of testing should be on the raw materials and packaging of cosmetics. If these two items fail to meet the standards, heavy metals will inevitably exceed the standard.

3. Other characterization method

There are many methods to figure out the venomous ions in makeups. Among them, atomic absorption spectrophotometry, inductively-coupled emission spectroscopy mainly about plasma and graphite furnace atomic absorption spectrometry is highly noteworthy. In this work, these three methods are also worth introducing.

3.1. Atomic absorption spectrophotometry

Atomic spectrometry is actually atomic absorption spectrophotometry. It uses the steam style method to absorb the ground state atoms of the elements. This first measured elements in the steam. This then detects the presence of heavy metal elements in the product by weakening the radiation's characteristic spectral line light [13]. The absorption law of light must be strictly followed in the implementation of the detection. The unique microwave digestion method is widely used in previous metal ions detection. And is the most popular of the three pretreatment techniques for detecting heavy metal elements in cosmetics. As it has a high level of reliability and requires less processing time than either wet digestion or dry digestion [13]. Atomic absorption spectrophotometry has good agility and will not be affected by many factors. Its use restrictions are not clear, and the sample is used more frequently and detected faster. Therefore, this method is widely used in detecting the content of heavy metals in cosmetics.

3.2. Plasma Emission Spectroscopy Based on Non Inductive Coupling

It is essential to make sure that the atoms being measured are in the excited state when utilizing emission spectrometry [13~14]. As a result, the detection method is widely utilized due to its high accuracy, good agility, high precision, and little matrix effect. However, there are still some unknown factors that will affect the detection process and results. Other elements may interfere with the detection elements, reducing its effectiveness. The spectrometer is growing its development towards simplicity, precision, and convenience in the future.

3.3. Graphite furnace atomic absorption spectrometry

This method is to place the sample in a large graphite tube and let a large current pass through the graphite tube. The graphite tube will heat the sample to a high temperature through three temperature rising procedures of drying, ashing and atomization to atomize the sample. The sensitivity of this detection method is relatively high, and the analysis speed is also more suitable. The detection equipment is easy to operate, and the maintenance of the equipments does not need too much investment.

4. Nanogold sensors

There are various methods for detecting heavy metal ions using nano gold sensors. The combination of AuNPs and DLS, the dynamic light scattering detection is a very promising analytical technology [15]. It does not involve complex separation steps and is more sensitive than other existing technologies. SERS, surface enhancement of Raman scattering is a rapid and non-destructive technology with high sensitivity, better specificity and no pretreatment, which can be directly used in field detection. SERS, based on citrate stabilized gold nanoparticles prepared from sodium citrate, overcomes the adverse effects of quenching caused by complex sample substrates. SERS also has the potential for multi group analysis.

As for SEF (metal nanoparticles with special configuration) detection, it has high specificity, good sensitivity, low cost. It can improve the optical stability of fluorescent molecules. It can also overcome the adverse phenomena such as self-quenching [19-21]. However, there are still some problems. Like how to reduce the calculation error between the estimated simulation value and the real value, and the way to achieve the perfect matching of the optimal light spread by the frequency of and the common frequency.

AuNPs gold standard strip is a typical rapid detection method. This does not need to buy heavy detection equipment, and has strong practicability. However, it will also have problems such as low repetition rate, false positive and false negative. And it's also unable for this method to detect multiple samples simultaneously.[22]

5. Conclusion

In recent years, as a promising material, nano gold sensor has become a research hotspot in finding the deleterious particles in cosmetics. In conclusion, this paper introduces the development history and mechanism of nano gold sensor in the checking reaction. In addition, by comparing with other detection methods, their respective advantages and disadvantages were elucidated. It is worth noting that nano gold test paper would win more development and research in the future due to its convenience and portable.

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