

GOLD IN THE PAST, TODAY AND FUTURE

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This paper deals with gold, which is described as a chemical element. Special attention is paid to its physical-chemical properties and, furthermore, where or in what form it can be found in nature. We discuss the role it has played through history and we inform how gold has been developed to the level it has reached today's value. Still more, when gold is broken into nanoparticles, this form could be highly useful for a wide range of processes, including general nanotechnology, electronics manufacturing and the synthesizing of different functional materials. It is important that we know that gold is also used in industry in many engineering applications (contacts in micro-electronics) and medicine (dental alloys, implants).

Key words: gold, physical-chemical properties, nano-particles, applications

Zlato u prošlosti, sadašnjosti i budućnosti. Ovaj članak govori o zlatu kao kemijskom elementu. Posebna pažnja posvećena je njegovim fizikalno-kemijskim svojstvima i gdje i u kojem obliku se može pronaći u prirodi. Razmatra se uloga koju je zlato odigralo u povijesti i donosi se informacije o tome kako je doseglo razinu vrijednosti koju ima danas. Zlato razlomljeno na nanočestice upotrebljivo je u širem spektru procesuiranja, uključujući opću nanotehnologiju, elektroničku proizvodnju i spajanje materijala raznih funkcionalnosti. Važno je znati da se zlato koristi i u industriji, mnogim inženjerskim procesima (kontakti u mikro-elektronici) i medicini (dentalne slitine, implantanti).

Cljučne riječi: zlato, fizikalno-kemijska svojstva, nanočestice, primjene

INTRODUCTION

Gold is a chemical element with the atomic number 79 and the symbol Au, which is derived from the Latin name "aurum" and means the morning dawn [1]. By coagulation it crystallizes in a centred cubic grid and in the periodic table it is located between the transition metals. The relative atomic mass of gold is 196,97, the density is 19,32 g/cm³, the melting temperature is 1063 °C, the elastic modulus is 77 MPa and the coefficient temperature of elongation (WAK) is 14,1 μm/m · K [1]. Gold is a very dispersed and rare element in the Earth's crust. In the wild it is located in its native form or (less frequently) in the form of telluride, which contains the only Golden minerals (kalaverit, sylvanite, petcit) [2]. Native gold is located primarily in the veins of silica (SiO₂), in the ores of other materials, or in deposits and is not clean; it contains 1–50 % mercury. The largest deposits of gold are in South Africa, the USA, Canada, Australia, Mexico and Russia. Approximately 20 % of world production is used commercially, while the rest is in gold reserves (the gold basis of paper money).

PHYSICAL-CHEMICAL PROPERTIES

Gold has its own unique yellow colour. Its appearance is also influenced by its brilliance and reflective ability. Because of these properties gold cannot be confused with any other metal. If gold contains an admixture of other elements it changes colour. Due to the admixture of silver in gold (up to 30 % by weight) it turns silver-white [3]. If the surface is polished the sharp metallic shine is stressed. Gold products are usually made of an alloy in which you can find behind the gold other alloying elements such as silver, copper, platinum, palladium etc. in many cases where products contain copper, so-called oxidation zones are visible, which is the reason for the dark, unpolished look of the surface [4]. Gold has almost twice the density of lead and 19,3 times greater than that of water. The admixture of other metals also has an effect on the density. For example, if the mass fraction of silver in gold alloy is between 2 and 20 %, then consequently the alloy density is between 15,5 and 19,3 g/cm³ [1]. Other contaminants which may affect the density are copper, platinum, palladium, rhodium, iridium and bismuth.

In the chemical sense gold is the least active metal, since it burns in air, is not oxidized in water, does not change colour, does not react with strong alkaline solutions and all the pure acids (except for selenium acid). Gold dissolved in a solution which is a mixture of chlorine and nitric acid (HCl: HNO₃ = 3:1); it dissolves in a

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cyanide solution [5]. Gold dissolves in mercury to form amalgam. The gold compounds have one (+1) or three (+3) valence and they are not very persistent. Colloids are formed by adding a solution of formaldehyde or phenylhydrazine to gold. Gold is a soft and very dense metal with a strong yellow colour and has a high degree of cleavage.

GOLD IN THE BANKING BUSINESS

In the fourth millennium (before Christ) the Egyptian workers found their first silver and gold. This discovery formed the natural exchange system of the economy at that time. Minted as indestructible silver and gold coins and precious metals they began to be used as currency. For security reasons, they began to be stored by the Goldsmith, and these in turn issued a Certificate of Safekeeping (CS), which was redeemable for silver and gold, and which later became the paper money used instead of silver and gold. On this basis they began subsequently to establish a private bank, and soon it was found to be in circulation longer than the CS as it was available in silver and gold. Later other currencies were developed which were also based on silver and gold, which corresponded to the supply of these precious metals as they were stable and not subject to inflation.

During the First World War huge financial resources were required to finance military operations. Because the war lasted a full four years, they violated the gold standard and printed more money than they had gold and silver. As a result, the uncovered amount of money has increased and inflation has started to show. In the fifties of the last century they tried to get back the gold standard, so all currencies were tied to the dollar, and this contains an ounce of gold, which at the time was 35 dollars. Today, gold stocks are at an end, the money in circulation is growing and is us only on the trust of its users.

GOLD IN NANOTECHNOLOGY

Nanoparticles lie between bulk and atomic dimensions and are therefore endowed with special properties, thereby making them starting material for many futuristic applications. The properties of nanoparticles depend on their crystallite sizes [6]. Therefore, control over the particle sizes and particle distributions (PSDs), is highly desirable. Of the different classes of organic and inorganic (metal, dielectric, and semiconductor) nanoparticles, noble metal nanoparticles have fascinated scientists' from historic times because of their unique size- and shape-dependent optical properties [7].

Today the potential of Au nanoparticles is recognised to derive from the addressability of their interesting optical properties via spectroscopic and photonic techniques [8]. For those spherical nanoparticles much smaller than the wavelength of light (diameter $d \ll \lambda$), an electromagnetic field at a certain frequency (ν) induces a

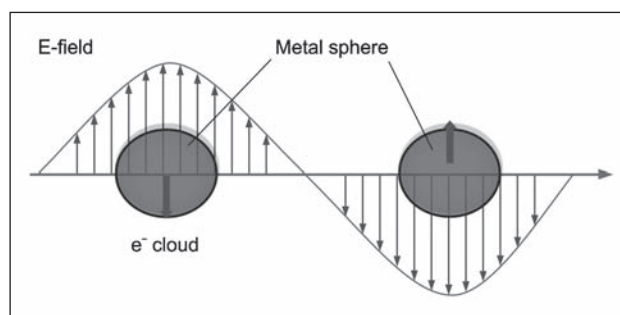


Figure 1 Schematic presentation of the interaction of a metal nano-sphere with light

resonant, coherent oscillation of the metal free electrons across the nano-particle (Figure 1). This oscillation is known as the surface Plasmon resonance [7,8].

The resonance lies at visible frequencies for Au metal. The surface Plasmon oscillation of the metal electrons results in a strong enhancement of absorption and scattering of electromagnetic radiation in resonance with the surface Plasmon resonance (SPR) frequency of the Au nanoparticles, giving them intense colours and interesting optical properties. The frequency and cross section of SPR absorption and scattering is dependent on the metal composition, nanoparticle size and shape, dielectric properties of surrounding medium/substrate and presence of inter-particle interactions. Au is the plasmonic metal of choice because of its much higher stability as compared to Cu and other metals. In addition, spherical Au colloids can easily be made in a wide range of sizes (4-80 nm) by facile chemistry involving the reductions of Au ions in solution [9]. Other interesting Au nanostructures (Figure 2) with modified optical properties e.g. nanorods, nanoprisms, triangular nanoparticles, nanocubes, and composite silica core Au-shell particles, can be fabricated via different techniques, such as: wet synthesis techniques, electrochemistry, photochemical techniques, nano-lithography, ultrasonic pyrolysis, etc.

Due to the phenomenon of SPR, the absorption and scattering cross-section of Au nanoparticles are signifi-

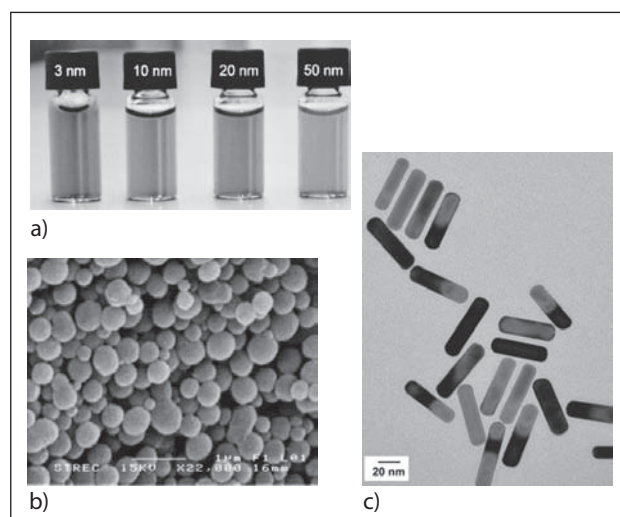


Figure 2 a) Photographs of colloidal dispersions of Au nanoparticles with increasing sizes, b) Au nanospheres, c) Au nanorods

cantly superior to the absorbing and fluorescing dyes used conventionally in biological and biomedical imaging [10]. Researchers demonstrated that the optical cross-sections of the Au-nanospheres are typically four to five orders of magnitude higher than those of conventional dyes. Current diagnostics and investigational techniques in molecular biology and biomedicine rely heavily on chemical contrast agents to stain/label specific cells and tissues of interest [11] in order to overcome the problem of weak signals of endogenous chromospheres and the subtle spectral differences between normal and diseased cells and tissues. Colloidal Au nanoparticles with strong SPR enhanced absorption and scattering are an important addition to the toolbox of imaging labels and contrast agents. Au nanoparticles are not susceptible to photo-bleaching and they appear to be biocompatible and non-cytotoxic, as supported by recent experiments on cells [11].

Another factor motivating the use of Au nanoparticles is their facile bio conjugation and bio modification [12]. The surface of Au nanoparticles has a strong binding affinity towards thiols, disulphides, and amines. In particular, the simple Au-thiol chemistry allows the surface conjugation of various peptides, proteins, and DNA. The electrostatic adsorption of biomolecules such as vitamin C and or large protein/enzyme molecules, to the nanoparticles' surface is a simple and commonly used technique for Au nanoparticles capped with citrate or similar carboxylic acid derivate.

GOLD IN DENTISTRY

Gold is the oldest dental restorative material, having been used for dental repairs for more than 4 000 years. These early dental applications were based on aesthetics rather than masticatory ability. The use of gold in dentistry remains significant today, with typical annual consumption estimated to be approximately - 70 - tonnes - worldwide. However, with an increasingly wide range of alternative materials available for dental repairs, it is considered appropriate to review the current gold based technology available today and thereby highlight the exceptional performance that competing materials must demonstrate if they are to displace gold from current usage.

In conservative and restorative dentistry, as well as in orthodontics, gold is used either as a pure metal, or alloyed together with noble metals and base metals. This use of pure gold is limited to direct filling of small occlusive cavities and no standard exists for the application and properties of direct filling with gold. However, pure gold used in this application is very soft (HV 25), has a very low 0,2 % proof stress (30 MPa), and a large elongation (45 %). As a result it can be cold worked very easily, a necessary requirement for filling a cavity precisely. Since gold fillings do not have high mechanical resistance against masticatory forces, they are only suitable for very small cavities. In recent years, pure gold has also been used through the electroforming

process. Electroformed inlays and onlays are suitable to be cemented into cavities after they have been veneered with porcelain. Tooth restorations such as porcelain veneered copings for crowns and bridgework can be electroformed with pure gold. Unfortunately, no standard yet exists for this process, which is rapidly becoming an established mainstream technique in modern dentistry. A more common technique in conservative dentistry is cementing investment cast gold alloy inlays and onlays into cavities.

Gold alloys are used in dentistry, not only for their preferred golden colour [13], but also because they maintain an extremely high chemical stability in the mouth. They also possess several desirable mechanical properties such as high strength, ductility and elasticity [14]. From among the various types of alloys used for porcelain fused to metal (PFM) restorations, Au-Pt based high noble alloys have had the advantage of being around for some considerable time. They are part of clinical experience and are extremely successful [13]. High Au-content dental alloys, including Au-Pt alloys, show good biocompatibility due to the corrosion resistance of high noble elements [13]. Besides functional performance and aesthetics, biocompatibility is a third important requirement for dental restorative materials. Where dental restorations are based on the use of different alloys, there is the obvious potential for oral polymetallism. Indeed, two alloys of different composition have different electrochemical potentials and inevitably induce corrosion, with the subsequent release of metal ions into the tissue. The ion release from metallic prostheses and implants is the main cause of any unwanted primary and secondary reactions in the human body. This phenomenon may lead to the deterioration of dental devices and, in the worst case, may cause prosthesis failure or fracture.

CONCLUSIONS

The Future of Gold is in the Biomedical Industry and Dentistry and is connected to the historical development work concerning the properties of gold. If longevity, functionality, aesthetics and biocompatibility, together with ease of manufacture, are considered as the most important requirements, the optimum material for biomedical applications and dental restorations is still a well-approved high gold alloy.

On the other hand there is the application of gold in nano-technology. Gold nanoparticles in the 1-10 nm size range have special physic-chemical properties that are useful in a wide variety of applications such as cancer diagnostics, catalysis, Raman and fluorescence spectroscopy selective, ionisation of biomolecules, and single electronics. In the future commercial realisation of such applications relies on economical synthesis of size-controlled nanoparticles, which requires the development of continuous-flow versions of lab-scale processes.

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