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CHARACTERIZATION OF GOLD NANOPARTICLES FOR VARIOUS MEDICAL APPLICATION

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In this contribution, we report the modified reduction synthesis of gold nanoparticles using trisodium citrate as a reducing agent and radical stabilizer. Both particle size and surface plasmon band are dependent on the reaction time. Scanning electron microscopic image and dynamic light scattering measurement shows that particles are spherical and monodispersed, respectively. This approach provides a simple route to fabricate gold nanoparticles that hold much promise for use in medicine and farmacy.

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1. Introduction

Materials in the nanometer size range may possess unique and beneficial properties, which are very useful for different medical applications including stomatology, pharmacy, implantology tissue engineering etc. Due to their attractive electronic, optical, and thermal properties; gold nanoparticles (AuNPs) have emerged with great interest, as well as catalytic properties, in the fields of physics, chemistry, biology, medicine, material science and some interdisciplinary fields [1-3].

Gold nanoparticles are widely used in immunohistochemistry to identify protein-protein interaction. However, the multiple simultaneous detection capabilities of this technique are fairly limited.

Gold metallic nanoparticles are commonly used in the lab as a tracer, to detect the presence of specific proteins or DNA in a sample. Gold nanoparticles have been used as a probe for the detection of various aminoglycosidic antibiotics like streptomycin, gentamycin and neomycin [4-5].

Such nanoparticles have proved to be adaptable, and so very useful [6-7]. Gold is used for nanoparticle applications because it is unreactive and is not sensitive to air or light. However gold does like to form bonds with itself and for this reason their surfaces have to be covered with a layer of protective molecules, for example sulfur compounds [8-9].

Researchers have recently used gold nanoparticles for identifying different classes of bacteria. At present for the identification of different classes of bacteria, expensive equipments are required. Further identification also requires lots of time as plating and culture is done on samples. This new technique of identification of different bacteria classes will be beneficial in medical diagnosis [10-11].

The many investigations showed that gold nanorods could be used to detect cancer stem cells [12]. The discovery is particularly valuable because cancer stem cells cause the out-of-control

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growth that makes malignant tumors so deadly. Besides being part of exhaustive tests that can detect cancers early on, nanoparticles may also form the basis of future cancer treatments. Lasers that react with gold nanoparticles could be used to destroy cancer cells. Or, nanoparticles could be used as targeted drug-delivery systems [13-14].

Gold nanoparticles (AuNPs) provide non-toxic carriers for drug and gene delivery applications that provide a useful complement to more traditional delivery vehicles. Their combination of low inherent toxicity, high surface area and tunable stability provides them with unique attributes that should enable new delivery strategies [15].

2. Experimental

2.1 Materials and methods

All chemicals were of reagent grade and used without further purification. Hydrogen tetrachloroaurate (III) trihydrate (0.21% solution) and trisodium citrate were purchased from POCh (Poland).

The SEM image was obtained on a JEOL JSM 7500F with BSE detector (Back Scaterred Electrons) and EDS (Energy Dispersive X-ray Spectroscopy). A drop of the sample solution was allowed to dry on a copper holder coated with chromium film.

Dynamic light-scattering measurements were performed in a Malvern Zetasizer Nano ZS apparatus (Malvern Instruments, Milan, Italy) at 25 ºC and started 2 min after the cuvette was placed in the DLS apparatus to allow the temperature to equilibrate. Measurements were carried out 24 h after the preparation of the suspensions.

UV–Vis spectroscopy measurements (330–700 nm) were performed using a Specord 205 at room temperature with a 1-cm optical length cuvette with a spectral resolution of 1 nm.

The FT-IR investigations were carried out with a Scimitar Series FTS 2000 Digilab spectrophotometer in the range of middle infrared of 4000-400 cm^{-1}, using the KBr pellet technique, which involves mixing thoroughly the material to be tested with KBr before forming a pellet at high pressure. 16 scans and the resolution of 4 cm^{-1} characterized these measurements.

2.2 Synthesis gold nanoparticles

The gold nanoparticles are prepared by sodium citrate reduction method [16] with modifications. The synthetic method developed for this experiment consistently produces a stable gold nanoparticles, provided the conditions are properly controlled. A 100 cm^3 aqueous solution containing 50 ppm $HAuCl_4$ and was put in a round-bottomed flask under reflux condenser and heated up to 65ºC. Then 0.5 cm^3 0.295 mol/dm^3 trisodium citrate was added at once and mixture was kept at this temperature during 3 hours without stirring. Just after mixing the color of the reaction mixture was light yellow and after several minutes was changed on pellucid black. The color of the solution slowly turned to ruby red indicating gold nanoparticle formation, which was confirmed by scanning electron microscopy. The suspension was stored at 4 °C.

3. Results and discussion

The formation of gold nanoparticles can be observed by a change in color since small nanoparticles of gold are ruby red. A layer of absorbed citrate anions on the surface of the nanoparticles keep the nanoparticles separated. The presence of this colloidal suspension can be detected by the UV-Vis spectroscopy (Fig. 1.)

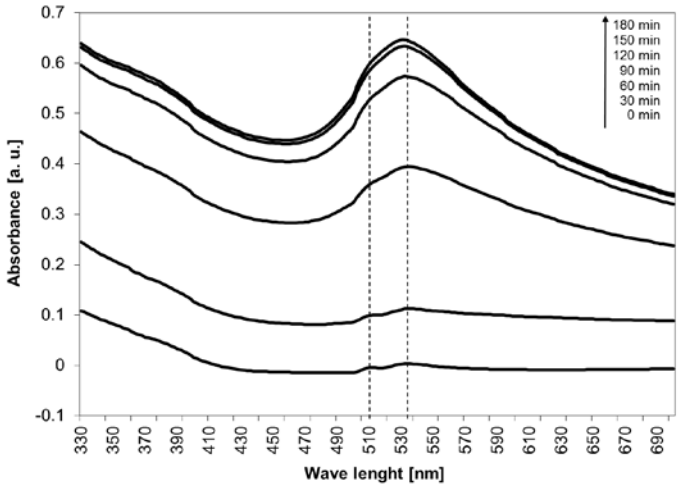

Fig. 1. Effect of reaction time on the UV-Vis spectrum of AuNPs

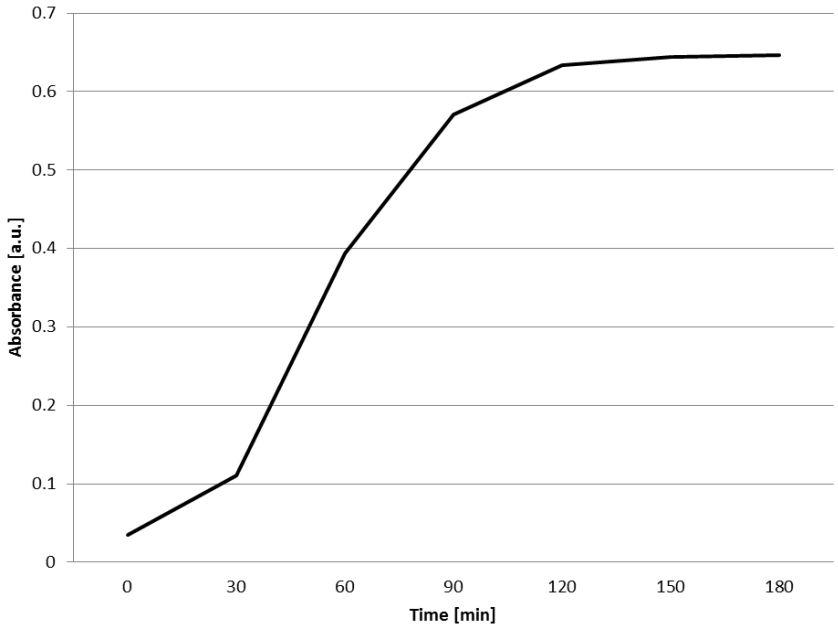

Fig. 2. The absorbance at 530 nm vs. reaction time

Our experiments showed that the reduction process was fairly slow. Fig. 1 shows the absorption band at 530 nm, is the characteristic SPB of gold nanoparticles [17]. But, there was very small shifting as well as broadening of SPB, which reveals the formation of gold nanoparticles with nearly constant size distribution.

The kinetics of the adsorption process was investigated by UV–vis spectroscopy in order to find a suitable time interval of self-assembling. Fig. 2. shows the absorbance at 530 nm arising from the plasma resonance of the colloidal gold nanoparticles increased gradually with the deposition time. It was found that maximum adsorption of colloidal gold nanoparticles obtained after about 150 min.

However, a little evidence of increase in size on long time reaction was observed, and this is probably due to the initially formed particle which serves as a nucleation site and as a result layer by deposition of gold takes place resulting in the increase in size. Also chemical reduction being a slow process the deposition was fairly slow. The result is quite similar as reported in seed mediated growth of gold nanostructures [18].

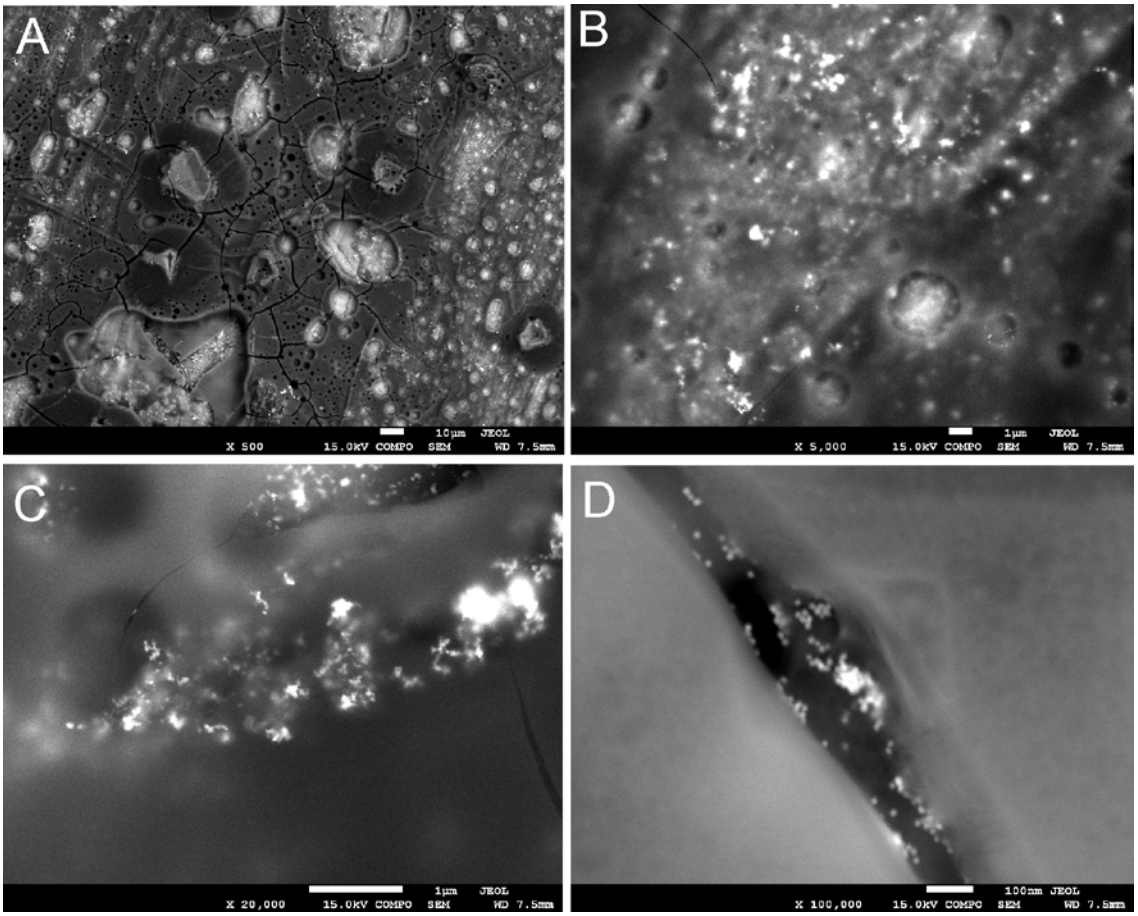

Fig 3. Representative SEM micrographs of gold nanoparticles with different magnifications

Fig. 3 shows the typical SEM-BSE images of the gold nanoproducts synthesized using above modified reduction process. As shown in Fig. 1D, the obtained nanoparticles have truncated sphere shapes. During the evaporation on the surface of zinc holder the gold nanoparticles form aggregate in a large cluster Fig. 1A-C.

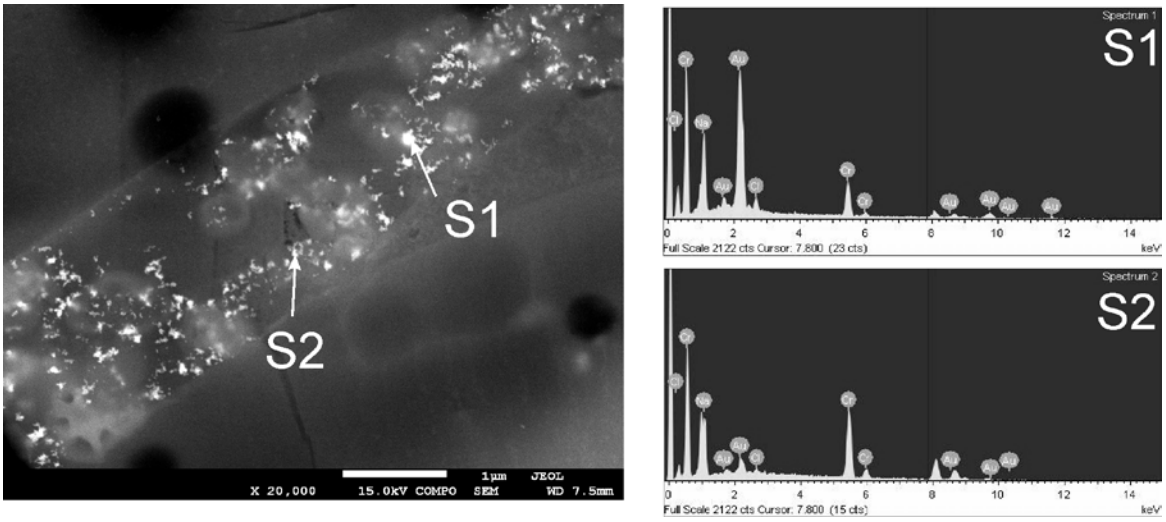

Fig. 4. SEM-BSE image and elemental analyses by EDS of AuNPs

EDS spectrum, linked with SEM, was used to analyze the element of gold nanoparticles (Fig. 4). In this analysis, the electronic beam is focused only on the gold aggregates, so the results can represent the real composition of a gold suspension. The EDS quantitative analysis confirmed that the gold content has the highest elementary composition, while chromium (film) has a minor content together with only a trace of zinc and sodium. Thus, the zinc signal came from the holder, while the carbon and sodium signals were from the sodium citrate.

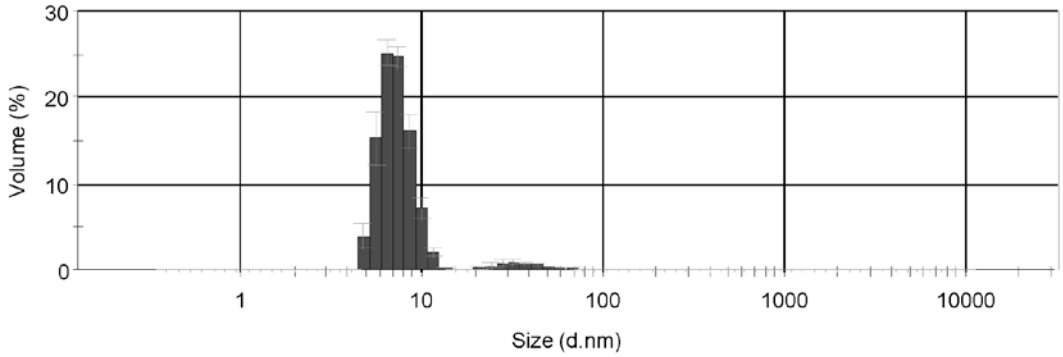

Fig. 5. The size distribution of aqueous Au nanoparticles.

In last decade, dynamic light scattering (DLS) has become popular method of measuring the size of colloidal nanoparticles [19]. Fig. 5 presents the gold particles size distribution determined by the DLS technique. The calculated particle size distribution by volume was included in the range of 3–22 nm (97% of AuNPs) .

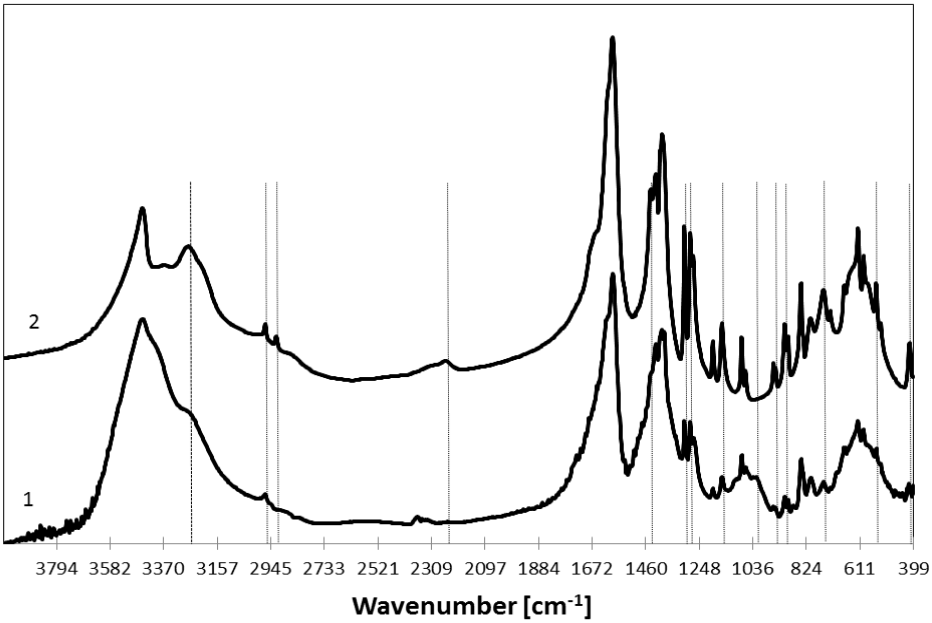

Fig. 6. FT-IR spectra 1- dried gold suspension, 2 - sodium citrate

Fig. 6. showed the characteristic FT-IR spectrum of dried gold suspension and trisodium citrate. It was obvious that the absorption band at about 3437 cm^{-1} is due to the hydroxyl ν(OH) stretching mode, and peak at 2308 cm^{-1} is because of the existence of CO_2 molecule in the air. The absorption appearing at 1587 cm^{-1} is due to ν(C=O) and at 1327 cm^{-1} can be assigned to ν(COO). Both samples show bands 2910 and 2934 cm^{-1} pertaining to symmetrical and asymmetrical stretching of methylene group. The absorption at 920 cm^{-1} can be ascribed to citrate precursor – $\gamma_r(CH_2)$ [20-21].

4. Conclusions

We have described the synthesis and characterization of surface-functionalized gold nanoparticles in order to develop a medical applications.

In conclusion, this work described an effective and modyfied reduction method for preparation of AuNPs using trisodium citrate as reducting agent and stabilizer.

According to the literatures [22] the distinct absorption peak from the surface plasmon absorption of the gold nanoparticles is located between 510 and 530 nm. The UV–vis spectra proved that the gold ions can be reduced by the sodium tricitrate in described conditions. The intensity of absorption increases with increasing time. During reaction time the absorbance at 530 nm underwent weak shift, indicating that the interlayer aggregation of gold nanoparticles is very weak during the 150 min of deposition. Also, nearly similar absorption around 530 nm supports significant similarities in cluster size.

Acknowledgements

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