Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 145 (2015) 280–288

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

A novel and greener approach for shape controlled synthesis of gold and gold–silver core shell nanostructure and their application in optical coatings

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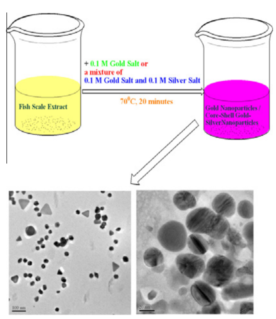
HIGHLIGHTS

- Design of a new simple and environmental friendly method employing the fish scale extract of *Labeo rohita.*
- Anisotropic, polyhedral and spherical gold nanostructures were formed by varying the reaction parameters.
- Bimetallic core–shell gold–silver nanostructures (spherical and oval shaped) were formed.
- The anisotropic gold nanotriangles were utilized in optical coatings.
- Gold nanotriangles were found to block the IR radiation and lower the temperature by almost 5 °C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 November 2014
Received in revised form 6 February 2015
Accepted 2 March 2015
Available online 9 March 2015

Keywords:
Green
Gold
Gold–silver
Nanostructures
Optical coatings

ABSTRACT

Green and facile synthetic methods have gained marvellous fame for the production of polyhedral, anisotropic and spherical gold, and gold–silver bimetallic nanostructures. The useful pivotal characteristics of a green procedure are the usage of environment benign solvent medium, reducing and stabilising agents, and shorter reaction time. We describe here a novel, and greener method for the production of gold and gold–silver core shell nanostructures using aqueous fish scales extract of the *Labeo rohita*. The effect of various reaction parameters, such as temperature and concentration for the synthesis of the nanostructures were studied. Results indicated that triangular and decahedron gold nanostructures were formed at a lower temperature (40 °C) and concentration (10%). While, icosahedral and spherical gold nanostructures were produced at a comparatively higher temperature (100 °C) and concentration (40%). The study also revealed that the core–shell bimetallic nanostructures with different morphologies (spherical and oval-shape) were formed at different ratios of chloroaurate and silver nitrate solution. Thus, the present study indicated a simple shape controlled synthesis of gold and gold silver core–shell nanostructures. The synthesised gold nanotriangles were coated over the glass substrate and found to be highly efficient in absorbing infra-red radiations for potential architectural applications. Therefore, the study demonstrated the facile usage of gold nanotriangles for optical coatings. The present strategy depicted the dual functional ability of the fish scale extract as reducing and stabilising agents. This strategy also eliminates the usage of hazardous chemicals, toxic solvents and harsh reducing and stabilizing agents.

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http://dx.doi.org/10.1016/j.saa.2015.03.059

Introduction

The need for developing environment friendly and sustainable procedures for the preparation of nanomaterials is urgently required. The researches all over the world aimed at adopting environmental benign starting materials, non-toxic solvents, environment friendly reducing and stabilising agents [1–3]. As a result, fast developments are seeking in the synthesis of metallic nanomaterials, especially gold and bimetallic (silver–gold) nanomaterials using environment friendly methods. These materials have wide applications in the field of sensors, electronics, catalysts and pharmaceuticals [4–6].

Various methodologies have been developed for the fabrication of noble nanomaterials of particular size and shape [7–10]. But all these methods are costly and harmful to the environment [11–13]. Hence, environment friendly methods, which are clean and non-toxic, have received enormous attention. Biosynthesis of nanomaterials is found to be one such method, which avoid or minimise the use of harmful substances. These include the utilization of microorganisms, such as fungi, bacteria, actinomycetes and whole plant [14–17]. However, these methods have certain disadvantages and cannot be employed for the large scale production. Hence, a better alternative method, which uses biogenic approach and gives rise to large scale production of nanomaterials is required. So, in this context, a waste material (fish scale extract of *Labeo rohita)* was utilized for the synthesis of gold nanostructures and gold–silver bimetallic nanostructures.

Fish scales are biocomposites of high ordered, type-I collagen fibres (41–84%) and hydroxyapatite $Ca_{10}(OH)_2$ $(PO_4)_6$ [18–20]. When the aqueous solution of these fish scales is heated, the collagen present in these scales get denatured to a mixture of random-coil single, double and triple strands [21]. These are accompanied by change in their physical and chemical properties, and may be due to collapse of the triple helical structure. Such modified collagen is called denatured collagen (gelatin) [22]. These collagens are made up of polypeptide chains containing amino acids in various compositions [23]. Various functional groups, such as $-NH_2$, $-SH$ and –COOH are also present in the collagens and endow them as a reducing as well as stabilising agent.

Hence, in this paper, we develop an eco-friendly, clean and facile method for the generation of Au-NPs and Au–Ag cores shell nanostructures using an aqueous extract of fish scales. These extracts are acting as reducing as well as stabilising agent. The effects of various reaction parameters, such as temperature, and concentration of the extract, in the synthesis of Au nanostructures were also investigated. Finally, the ability of the gold nanostructures (triangular) to act as a building block in the absorption of NIR-absorbing coatings is analyzed. The present synthesis process and the application of the gold nanotriangles are simple, environment friendly and robust.

Experimental details

Materials

Hydrogen tetrachloroaurate monohydrate ($HAuCl_4{\cdot}H_2O$), and silver nitrate ($AgNO_3$) of A.R Grade were purchased from Sigma–Aldrich. Double distilled water was used in all the experiments.

Preparation of fish scale extract

6 g of *L.* rohita fish scales were thoroughly washed and boiled at 60 °C for 20 min in 150 ml double distilled water. The resulting solution was filtered and used for further experiments.

Synthesis of gold nanoparticles

A 20 ml of 0.1 M aqueous solution of hydrogen tetrachloroaurate monohydrate was taken in a container and 20 ml of different concentrations of fish scale extract (10%, 20%, 30% and 40%) were added separately. These mixtures were then heated at 70 °C for 20 min followed by slow cooling of the solutions at room temperature. The solution was then allowed to stabilize for 1 day. After 1 day, the solutions with ruby red sediments were formed at the bottom of the container which indicated the presence of Au NPs. These were then centrifuged, filtered and the residues were washed several times with double distilled. Also samples of Au NPs were prepared by adding 20 ml of 0.1 M aqueous solution of hydrogen tetrachloroaurate monohydrate to 20 ml of 10% of fish scale extract and heating at different temperatures (40, 60, 80, and 100 °C), separately.

Synthesis of bimetallic gold silver core shell nanoparticles

Au–Ag bimetallic nanoparticles were synthesised by simultaneous mixing of 0.1 M aqueous solution of hydrogen tetrachloroaurate monohydrate and 0.1 M aqueous solution of silver nitrate in the ratio of (4:1, 3:2, 2:3, and 1:4) with 20 ml of fish scale extract at 70 °C for 20 min. The solution was then allowed to stabilize for 3 days. After 3 days, the solutions were centrifuged, filtered and the residues were washed several times with double distilled water to remove unbound polymers.

Characterization of the nanoparticles

The UV–Vis absorption spectra of the synthesized nanoparticles were recorded on Cary 100 Bio spectrophotometer (λ max in nm) equipped with 1-cm quartz cell. The TEM, HR-TEM images, and SAED pattern were recorded using JEOL-JEM 2100 transmission electron microscope operated at an accelerating voltage of 200 kV. The TEM samples of the nanoparticles were prepared by placing the solution drops over the carbon coated copper grids and allowing the solvent to evaporate at room temperature. The FTIR spectra were measured using Bruker Hyperion 3000 FTIR spectrometer, using thin, transparent KBr pellets prepared by pressing a mechanically homogenized mixture of dried sample with dehydrated KBr. The XRD pattern was recorded using a Phillips X'Pert Pro Diffractometer with CuKα radiation of wavelength 1.5418 Å.

Coating of the synthesised gold nanostructures

The synthesized gold nanostructures (spherical and triangle) were coated on the window opening of dimension 2 cm × 2 cm made of glass within an enclosed box of cardboard of dimension 10 cm × 10 cm × 10 cm. These were irradiated with a 250 W tungsten filament IR lamp kept at a distance of 20 cm from the box. The cooling due to IR absorption by the glass substrate coated with gold nanostructures [spherical (7 mg/cm^2) and triangular (single layered (4 mg/cm^2) and triple layered (13 mg/cm^2)] were studied by measuring the variation in temperature within the enclosed box as a function of time.

Results and discussion

UV–Visible analysis

Au NPs exhibits a unique UV–Visible absorption band derived from collective oscillation of conduction electrons upon interaction with electromagnetic radiation, which is known as localised