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ORIGINAL ARTICLE

# Green synthesis and characterization of gold triangular nanoprisms using extract of *Juniperus communis* L.

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## Abstract

In this study, we report the green synthesis of gold nanoparticles (AuNPs) with the use of easily available, safe to handle juniper extract (*Juniperus communis* L.) as a reducing and stabilizer agent. The AuNPs were characterized by UV–Vis absorption spectroscopy, atomic force microscopy (AFM), and transmission electron microscopy (TEM). Their growth was examined by UV–Vis spectroscopy over 24 h during storage at room temperature. Absorption measurements showed that the plasmon resonance wavelength appears around 530 and 700 nm. Electron-dispersive X-ray analysis (EDX) and selected area electron diffraction (SAED) of AuNPs evidenced the presence of Au (fcc) phases. TEM analysis showed spherical AuNPs and gold triangular nanoprisms. Differences in size and shape of the AuNPs were observed. ATR–FTIR confirmed the typical functional groups of polyphenols and their oxidation products on the AuNPs' surface.

**Keywords** Gold nanoparticles · Phytosynthesis · Juniper · Plasmonic materials · Transmission electron microscopy

## Introduction

In the recent decade, anisotropic nanomaterials have become important, since the shape of metal nanoparticles (NPs) plays a key role in different applications (Sajanlal et al. 2011; Goncharenko et al. 2018). Biocompatibility and non-toxicity of gold metal make gold NPs (AuNPs) solutions a favorable environment for biomolecules (Schmid 1992). The anisotropic AuNPs, wires, rods, prisms, and stars are efficient surface agents for the enhanced Raman spectroscopy (Rosi and Mirkin 2005), what made them highly appreciated and prospective material applicable in medicine.

The last few years have witnessed remarkable attention to the synthesis of non-spherical metal NPs (Hao et al. 2004; Beeram et al. 2010; Osberg et al. 2012; Payne et al. 2014; Al-Akra et al. 2017; Lopatynskyi et al. 2018). Based on the gathered knowledge, currently, the existing methods for Au nanoprisms synthesis require a shape-directing surfactant. Among these, a hazardous cetyltrimethylammonium bromide is still recognized as the most predictable surfactant, in relation to control of crystallinity, size, and shape of NPs, although Pelaz et al. (2012) reported, for instance, on good results with less harmful substances like sodium thiosulfate and polyethylene glycol. Another method applies the chemical reduction of $Au^{3+}$ with sodium borohydride, hydrazine hydrate, or ethylene glycol what increases NPs' toxicity either.

Biological systems have been already frequently used in the synthesis of NPs, for example, plant extracts used for synthesis of metallic NPs published by Teimouri et al. (2018) and Geraldes et al. (2016), with the purpose to eliminate hazardous reagents and focus on the utilization of NPs in humans. Such a green chemistry approach becomes an innovative way in the development of alternative protocols to prepare also much desired metallic nanoprisms. In plant extracts, a vast number of substances or group of

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components, such as vitamins, amino acids, enzymes, polysaccharides, and organic acid salts (citrates), can work both as reducing and capping agents in the NPs' synthesis. The existing number of plant species gives infinite possibilities in this field. Although the applications of plant extracts have unfolded a fresh era in the fast and non-poisonous techniques to produce AuNPs, the chemical processes are, indeed, complicated and obscure, yet. Nevertheless, the possibility of phytosynthesis of non-spherical AuNPs has been reported in many studies (Klekotko et al. 2017; Deokar et al. 2018; Waclawek et al. 2018). Despite extensive studies that were conducted in non-spherical AuNPs' synthesis, there are still many unknown factors which may affect the synthesis. For example, a major problem deals with the selection of a proper active substance to be used for gold reduction and for stabilization and controlling of the shape and size of the synthesized NPs. In general, there is no clear evidence which, of the multitude plant substances or a stereochemistry, suits the best for this or that NPs' shape and size.

The genus *Juniperus* includes roughly 68 species and 36 varieties, and only *Juniperus communis* L. growths widely in both hemispheres (Adams and Pandey 2003). In addition to essential oils (0.4–1.9%), tannins (3–5%), sugars (30%), and flavonoids (Fejér et al. 2018), berry cones of *Juniperus* contain polyphenols, polyphenol esters, and monoterpenes (Ochacka et al. 1997; Elmastaş et al. 2006).

To our best knowledge, the phytosynthesis of precious metal NPs using juniper extracts was published in a few reports only. Successful syntheses of silver NPs (AgNPs) using aqueous extracts of different juniper species were reported by Puiso et al. (2014) (*Juniperus communis* L.) and Ibrahim et al. (2018) (*Juniperus procera*). While the study of Puiso et al. (2014) was mostly dedicated to microbiological testing of AgNPs, the study of Ibrahim et al. (2018) was concentrated on the characterization of NPs and on the formation of both spherical and cubic AgNPs with an average size between 30 and 90 nm. AuNPs were obtained using water extract of *Juniperus communis* L. by Geraldes et al. 2016. Most of the obtained NPs were spherical with the minor presence of hexagonal shapes.

Herein, we report, for the first time, a simple, fast, and cost-effective synthesis of Au nanoprisms with aqueous ethanol extract of *Juniperus communis* L. as an efficient reducing, capping, and shape-directing agent.

## Materials and methods

### Materials

The juniper ripe berries (*Juniperus communis* L.) were collected in the calc-tuff locality of Spišský hrad in the eastern region of the Slovak Republic (N48°59.893′, E20°46.328′, altitude 590 m) during the third decade of September 2015. Collected berries were naturally dried. Chloroauric acid ($HAuCl_4 \cdot 3H_2O$, 99.9%) was purchased from Sigma-Aldrich. Before experiments, all laboratory glassware was cleaned with *aqua regia* solution (HCl:$HNO_3$ of 3:1) and rinsed with double-distilled water (DDW).

### Synthesis procedures

#### Preparation and characterization of extract

5 g of dried berry cones were crushed in a porcelain mortar with a pestle and macerated in 100 mL of 70% ethanol. Room-temperature extraction was completed after 72 h. Fast filtering of the obtained extract was performed with a filter of type KA 1-M (Papírna Pernštejn s.r.o., Czech Republic). To measure the dry matter content in the aqueous ethanol extract, we used a Shimadzu MOC-120H moisture balance. The total phenol content was determined with the Folin–Ciocalteu reagent (FCR, Merck), according to a procedure described by Singleton et al. (1999).

#### Preparation of gold nanoparticles

Synthesis of AuNPs was performed at an ambient air temperature of 20–23 °C by the direct interaction of plant extract and aqueous $HAuCl_4$ solutions under continuous stirring. Different volumes of the extract in the $HAuCl_4$ solutions with varying concentrations were tested to find the best result. Briefly, 0.1–0.2 mL of the extract was added to 3.8–3.9 mL of 0.1–1.0 mM $HAuCl_4$ aqueous solution, followed by 24 h incubation in the dark at room temperature under continuous stirring. The kinetics of the AuNPs formation was followed by ultraviolet–visible (UV–Vis) spectroscopy. When the reaction ceased, the resulted AuNPs were centrifuged, and the pellet was re-suspended in DDW.

### Characterization

UV–Vis spectra were collected by Shimadzu UV-1800 spectrophotometer with matched 1-cm quartz cells. Attenuated total reflectance Fourier transform infrared (ATR–FTIR) spectra were acquired with a Shimadzu Prestige 21 instrument equipped with a single reflection accessory and ZnSe ATR crystal (PIKE Technologies, USA). Transmission electron microscopy (TEM) imaging was conducted with a JEOL JEM-2100F microscope equipped with attachments for electron-dispersive X-ray analysis (EDX) and a GIF TRIDIEM post-column energy filter for the acquisition of energy-filtered images and selected area electron diffraction (SAED). TEM specimens were prepared by dropping a sonicated aqueous suspension of AuNPs on a carbon-coated copper grid and followed with drying it under the infrared

lamp. TEM images of different magnifications were captured at a maximum acceleration voltage of 200 kV. Selected nanometer-sized object was imaged by atomic force microscopy (AFM) with a commercial Nanoscope III instrument (Digital Instruments, Santa Barbara, CA).

## Results and discussion

Figure 1a shows *Juniperus communis* L., a plant species well known as a rich source of polyphenol compounds. We recognize aqueous ethanol extract of berries as a prospective resource for the preparation of AuNPs. The extract prepared in this study contained 24.06 mg/mL (±0.15 mg/mL) of dry matter and 23.25 mg GA/g in dry matter (eq. of gallic acid) of polyphenols.

The reaction mixture during the synthesis changed its color, because the AuNPs formed gradually. This gradual formation was detected also by UV–Vis spectrometry in the reaction mixture (Fig. 1b, c). Typically, the extinction spectra revealed two bands of surface plasmon resonance (Fig. 1c). The first plasmon resonance peak from spherical-shaped AuNPs is at 535 nm. The second peak sourced the anisotropic AuNPs shifts towards the infrared range. As shown in Fig. 1c, this significant peak at about 700 nm distinctively shows only at a certain volume ratio of extract and $Au^{3+}$ ions; however, we cannot discount the presence of anisotropic AuNPs also in the other reaction mixtures.

Based on the spectral analysis, we conclude that, in the mixture with low-concentrated reactants, mainly spherical AuNPs were formed, while, in solutions with middle and high concentrations of reactants, anisotropic AuNPs were formed in addition to spherical ones. Still, in all solutions, spherical AuNPs prevailed over anisotropic.

Concerning the best result, the highest concentration of anisotropic AuNPs was observed at a ratio of the reactants of 0.2 mL of the juniper extract and 3.8 mL of 0.50 mM of $HAuCl_4$ (0.5 mM, spectrum blue line—Fig. 1c). Further increase of $Au^{3+}$ concentration leads to appearance of multidisperse NPs what is clearly seen as broadening of surface plasmon resonance band in UV–Vis spectrum (0.75 mM, spectrum purple line—Fig. 1c).

In general, concentrations of the reagents influence the reaction rate. In this respect, we conducted a series of prolonged experiments where the interaction of the extract with $HAuCl_4$ solution was monitored hourly by the UV–Vis

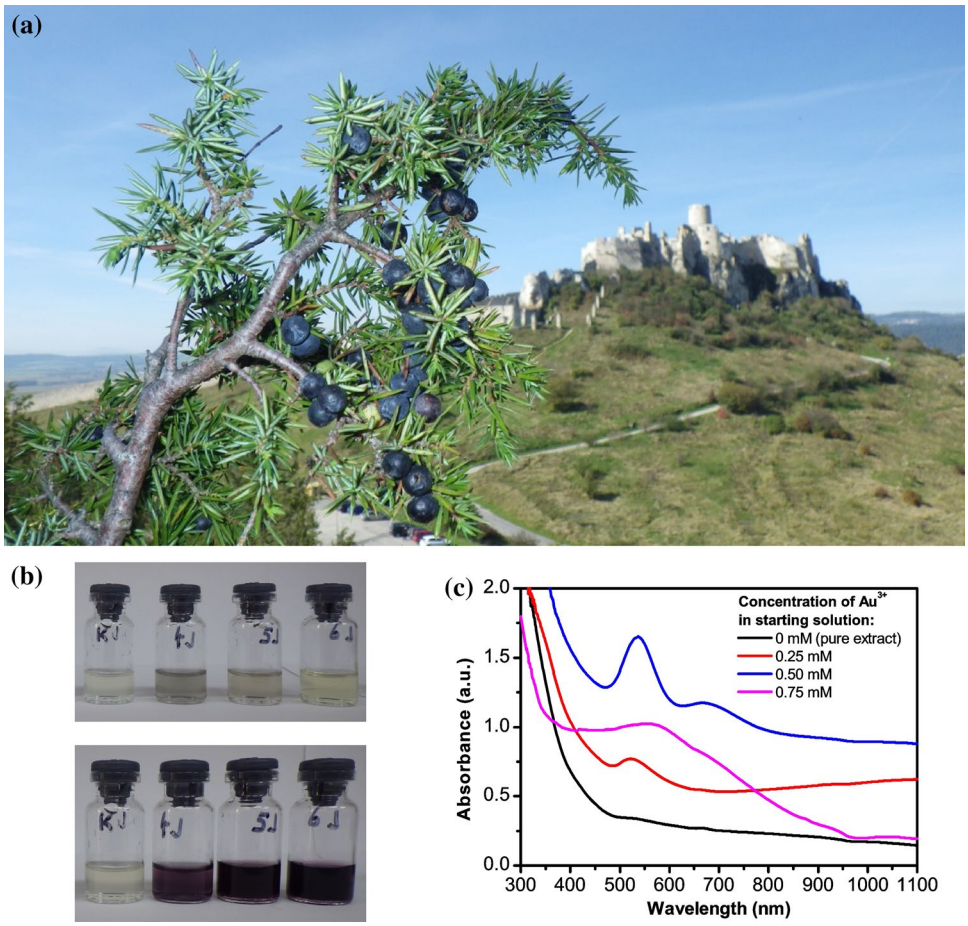


**Fig. 1** **a** *Juniperus communis* L. at the locality, **b** aqueous ethanol solutions containing AuNPs prepared using juniper berries extract, and **c** UV–Vis spectra of the extract and solutions

measurements (Fig. 2). As was expected, the reaction rate correlated with the concentration of reactants. Regardless of the amount of extract, the formation of solely spherical nanoparticles was observed for the reacting solutions with a relatively low concentration of $HAuCl_4$ (0.25 mM). In contrast, the non-spherical nanoparticles were formed only if the concentration of $HAuCl_4$ was at least 0.50 mM.

In general, the growth of AuNPs was completed no longer than in 10 h (Fig. 3). However, in the case when reacted 0.2 mL of the extract with 0.50 mM $HAuCl_4$ solution, the reaction ceased even in 5 h. An unexpected behavior associated with the rate of AuNPs' formation at low concentrations of the extract and $Au^{3+}$ ions. In such a case, the phytosynthesis ran faster than for the more concentrated reactants. Probably, this is because of varying the formation rate for that AuNPs having different shapes. In the beginning, we most likely see the fast formation of spherical AuNPs followed by the slower formation of anisotropic AuNPs what is clearly observed for the reaction mixture with the higher concentration of $Au^{3+}$ ions.

The role of polyphenol compounds in the formation and stabilization of metal nanoparticles has been discussed in several reports (Lee et al. 2011; Kumar et al. 2013). The common idea is that the hydroxyl groups (OH) are partially oxidized to polyketones and polyaldehydes that are, subsequently, the AuNPs' stabilizers. The comparison of the FTIR–ATR spectra supports this hypothesis (Fig. 4a). The high concentration of polyphenols in the extract confirms the presence of OH-groups (3100–3400 $cm^{-1}$), aliphatic C–H bonds (2840–2930 $cm^{-1}$), aromatic C=C bonds (1607 $cm^{-1}$), and C–H bending (1450–1465 $cm^{-1}$).

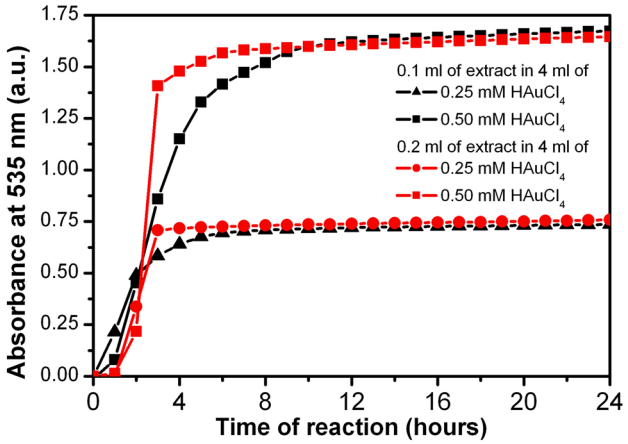


**Fig. 3** Kinetics of AuNPs' formation

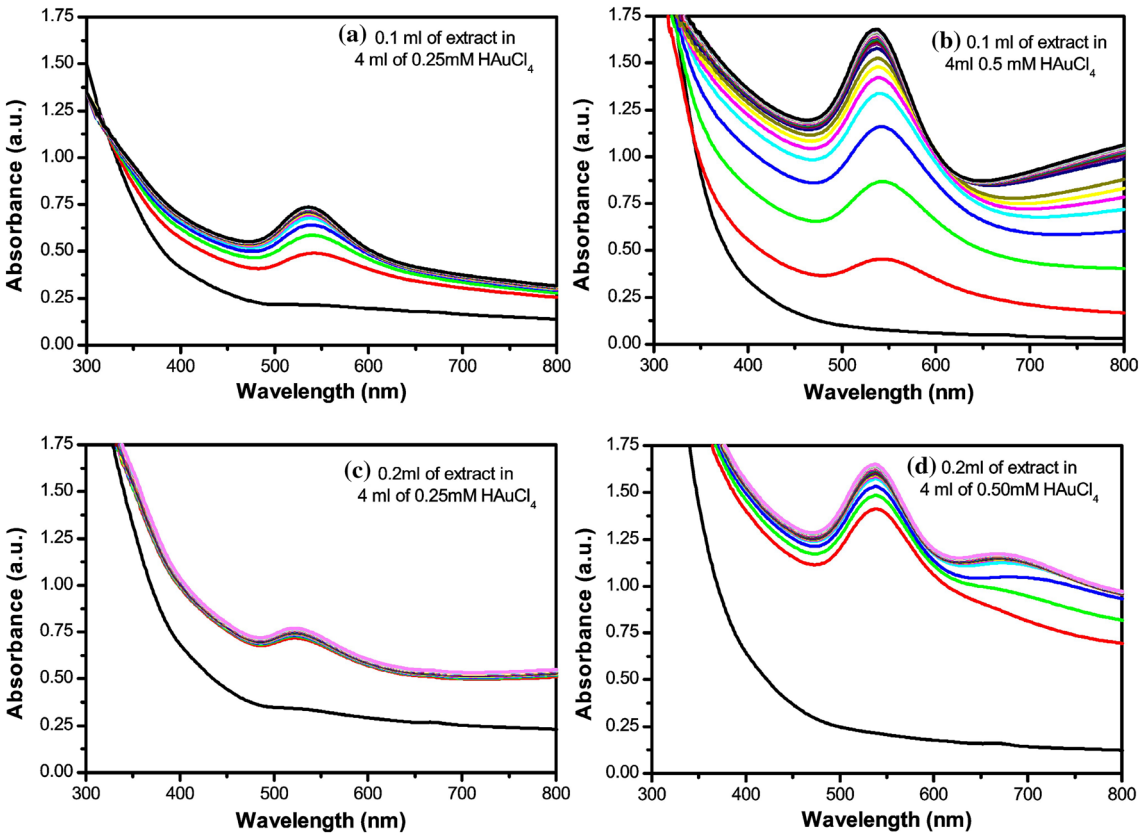


**Fig. 2** **a–d** UV–Vis spectra of AuNPs recorded with a time step of 1 h

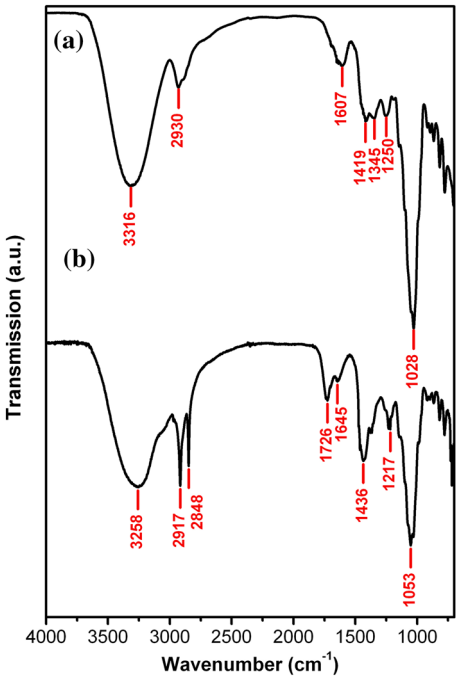


**Fig. 4** ATR–FTIR spectra of **a** extract of *Juniperus communis* L. and **b** AuNPs

Absorption at 1020–1060 $cm^{-1}$ and 1436 $cm^{-1}$ is from the stretching vibrations of C–O–C bonds; absorption at 1217 $cm^{-1}$ corresponds to the vibrations of C–O bonds. On the other hand, the spectrum of AuNPs showed certain changes in absorbance (Fig. 4b). The increased absorption at 1726 $cm^{-1}$ correlates with the supposed increase of the C=O bonds produced by the oxidation of phenol groups. The strong band appears at 1053 $cm^{-1}$ which one can ascribe to the stretching vibration of C–O.

Figure 5 combines the results of TEM and AFM observations on the formed NPs. It is important to remark that the TEM images were captured directly from the original product; neither size selection nor any purification process was applied. A simultaneous presence of spherical particles (diameter of up to 10 nm) and triangular nanoprisms (side size of 15–20 nm, with larger maximal size of 50 nm), which gold origin is confirmed by the EDX analysis (Fig. 5c), is supported by the plasmon resonance peaks at 535 and 700 nm (Fig. 1c). The broad extinction band, in the range of wavelengths from 650 to 800 nm, should be mostly from the triangular Au plates (nanoprisms), which are the second largest morphologic group in the AuNPs mixture. However, due to the presence of some other shapes of the AuNPs, visible in the TEM images, we assumed that this band corresponds to all the anisotropic structures presented in the solution. The size of the triangular nanoprisms varies from 10 up to 50 nm, and the thickness is up to 0.8 nm. Insert in Fig. 5a portrays the typical SAED patterns measured by focusing the electron beam perpendicularly on the flat surface of a typical triangular plate. The SAED spots exhibit the set of hexagonally symmetric patterns. Six heavy white spots correspond to the {220} reflections of the face-centered-cubic (fcc) Au orientated in the [111] direction, as one can see from TEM image with an observed interplanar spacing of 0.233 nm (Fig. 5b).

The above-obtained results confirm the important role of polyphenolic compounds in the formation and stabilization of NPs. Here, the choice of solvent for extraction influences significantly composition of the extract, i.e., diversity and quantity of components leached from plant material. Our results confirm that aqueous ethanol extraction of *Juniperus communis* L. is effective for preparation of non-spherical AuNPs more than the aqueous extract used in the study published by Geraldes et al. 2016.

## Conclusions

An easy green protocol is proposed for the synthesis of AuNPs. Different ratios of the aqueous ethanol extract of *Juniperus communis* L. and $HAuCl_4$ were applied to obtain the prismatic shaped AuNPs. However, only the spherical AuNPs can be synthesized within a low concentration of reactants. At higher concentrations, the triangle-shaped AuNPs with the size up to 50 nm can be prepared. The kinetic experiments have shown that the growth of AuNPs is completed in 5 h at room temperature. ATR–FTIR spectral analysis proves the presence of hydroxyl, carbonyl, and carboxyl groups on the AuNPs surface. Increasing absorbance of the carbonyl bonds in the ATR–FTIR spectra of AuNPs confirms the significant role of polyphenols of the plant extracts in the self-organization and stabilization of metal NPs.

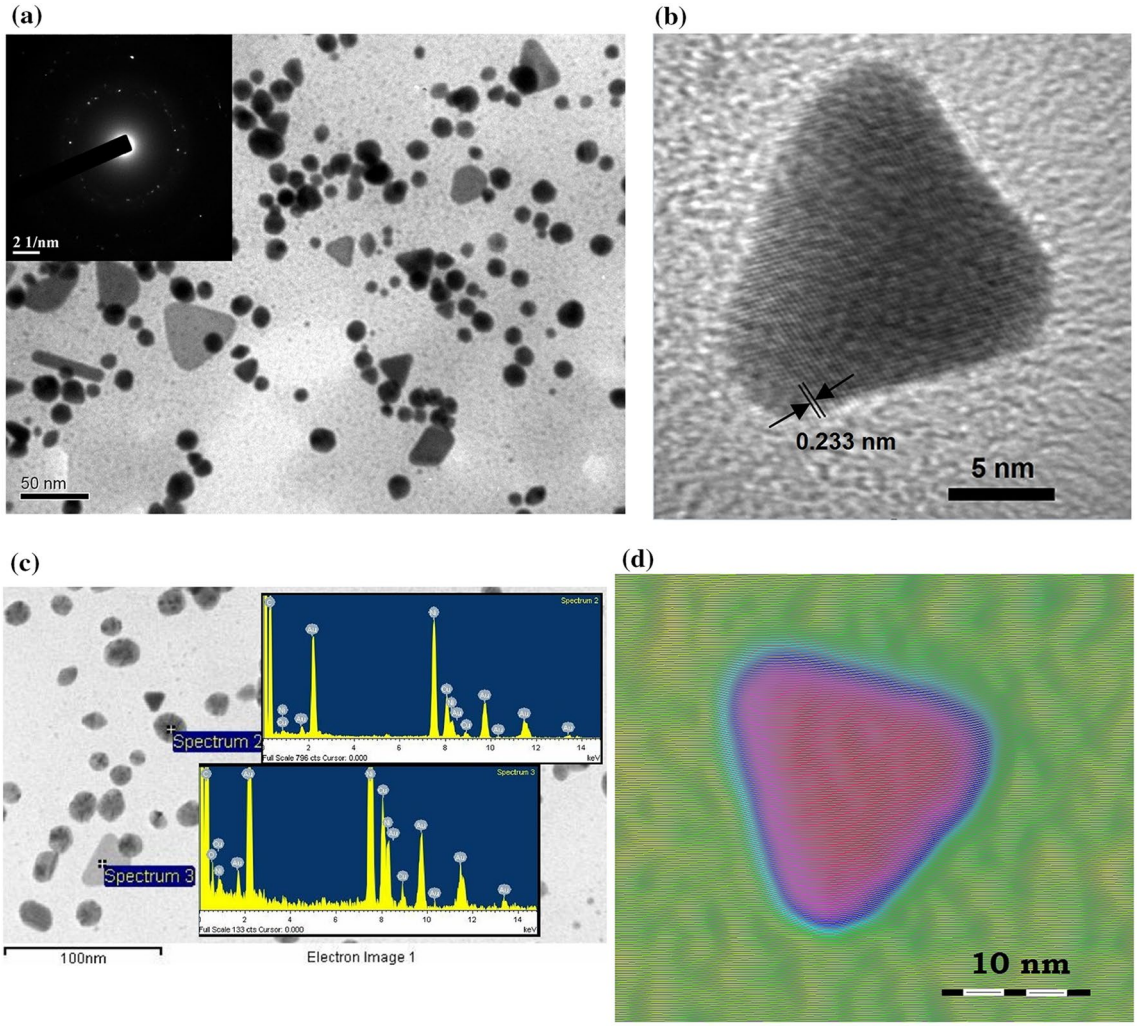


**Fig. 5** TEM **a**–**c** images and **d** tapping-mode AFM image of AuNPs synthesized using the extract of *Juniperus communis* L.: **a** spherical and **b** prismatic AuNPs. Inserts in **a** SAED pattern and in **c** EDX analysis

## Compliance with ethical standards

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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