PHYTOSYNTHESIS AND PROPERTIES OF NON-SPHERICAL GOLD NANOPARTICLES

Mariychuk R.[1], Grishchenko L.M.[2], Linnik R.P.[2], Lisnyak V.V.[2]

[1] Department of Ecology, Faculty of Humanities and Natural Sciences, University of Prešov in Prešov, 17th November Str. 1, 08001, Prešov, Slovakia
[2] Faculty of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska Str. 62a, 01601 Kyiv, Ukraine
E-mail: ruslan.mariychuk@unipo.sk

Abstract. Phytosynthesis of gold nanoparticles (AuNPs), synthesis using plant extracts, delivers not only such impressive benefits like simplicity, cost- and time-effectivity, but also biocompatibility, which is important for application of nanoparticles in biology and medicine. However, the plant extracts are known as very complicate systems. Therefore, in this study we were focused on the phytosynthesis of Au NPs using extracts of *Melissa officinalis* L. and *Mentha piperita* L. prepared at different extraction conditions: solvent (water, ethanol, and acetone), temperature, concentration with aim to optimize the protocol of synthesis with high yield on non-spherical AuNPs. Characterization of AuNPs was carried out using UV-Vis spectroscopy, ATR FTIR spectroscopy, and electron microscopy.

Introduction. The recent decade is marked by extensive studies in the fields of preparation, investigation of nanomaterials, and attempts of their application in different areas. Metallic NPs are a special class of nanomaterials with observed to be prospective for utilization in catalysis, sensing, medicine, electronics, etc. Therefore, there is a huge interest in the development of new, eco-friendly, cost- and time-efficient protocols for the preparation of NPs with controlled size and shape. Control over the shape of NPs allows changing the optical properties of NPs and opens the possibility to use them in surface-enhanced Raman spectroscopy, drug delivery systems, optical photo-thermal therapy, etc.
Numerous studies in the field of phytosynthesis of AuNPs show that some extracts are suitable for the synthesis of spherical NPs [1]. But in other cases, extracts of some plants contain the components which support the formation of other shapes, like nanotriangles, nanohexagons, nanostars, nanorods, etc. [2].

The aim of this study was synthesis and characterization of AuNPs prepared using extracts *Melissa officinalis* L. and *Mentha piperita* L. with high concentration of non-spherical AuNPs.

Experimental. Plant material was collected on experimental field of Prešov University, Prešov, Slovakia.
1. Extracts of *Melissa officinalis* L. and *Mentha piperita* L. (Slovak variety *Kristinka*) were prepared from air dry leafs using various extraction conditions: solvent (water, ethanol, and acetone), temperature (4-100 °C), concentration.
2. Syntheses of AuNPs were carried out by direct interaction of plant extract (various concentrations) and 1 mM $HAuCl_4$.
3. UV-Vis spectra were collected using Shimadzu UV-1800 spectrophotometer.
4. Infrared spectra were measured using Shimadzu FTIR Prestige-21 spectrometer with PIKE ATR accessory on Ge crystal.
5. Extract's dry matter contents was measured using Shimadzu MOC-120H moisture analyser.
6. Transmission electron microscopy images were captured on a JEOL JEM-2100F transmission electron microscope at a maximum acceleration voltage of 200 kV.

Results and Discussion. The plants of mint family (Lamiaceae) are known as source of aromatic compounds. However, their extracts also often tested as efficient reducing and capping agents for the phytosynthesis of silver and gold NPs [3, 4]. Since, the plant extracts are complex chemical system, numerous studies are focused on the understanding of roles of different components on the formation NPs, control of stability, size and shape of NPs.
In this study, we have prepared extracts of *Melissa officinalis* L. and *Mentha piperita* L. at different extraction conditions – solvents (water, water-ethanol, water-acetone) at different temperatures. Organic solvents of extracts were removed by vacuum evaporation (ethanol) or liquid-liquid extraction (acetone). So, all final extract were aqueous.
Despite the different plants, FTIR spectroscopy measurements have shown the similarity of functional groups in obtained extracts (Fig. 1). This confirms that components of extracts belongs to polyphenolics with high reducing properties.
UV-Vis spectroscopy was applied to obtain previous information about formation of spherical (with SPR maximum at ca. 560 nm) and non-spherical AuNPs (second SPR maximum in NIR region). It was observed that AuNPs prepared using same extract to Au^{3+} ratio (1mg/ml : 0.75mM $HAuCl_4$) have shown the different profiles (Fig. 2). The presence of SPR maximum was observed in all samples. However, the position of second maximum heavily depends from the applied extract.

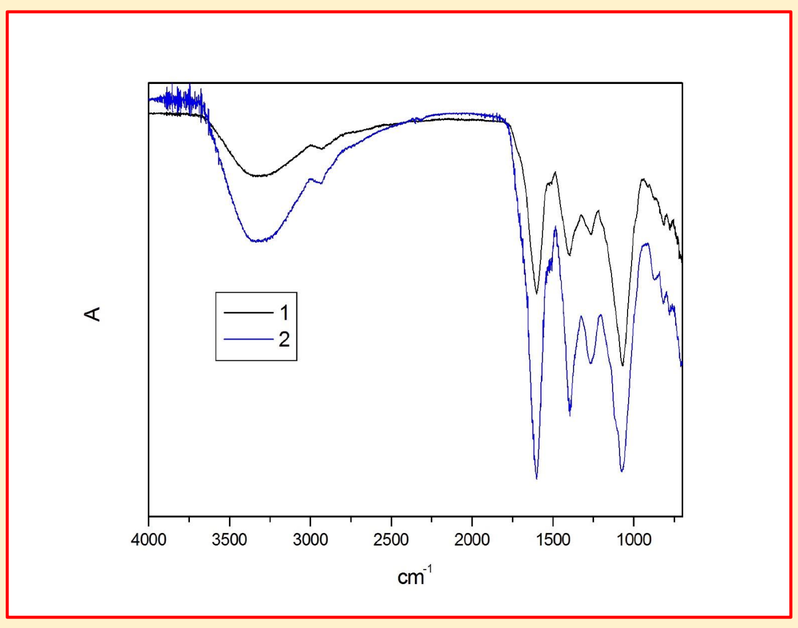

Figure 1. FTIR ATR spectra of extracts of :
1 - *Melissa officinalis* L.;
2 - *Mentha piperita* (variety *Kristinka).*

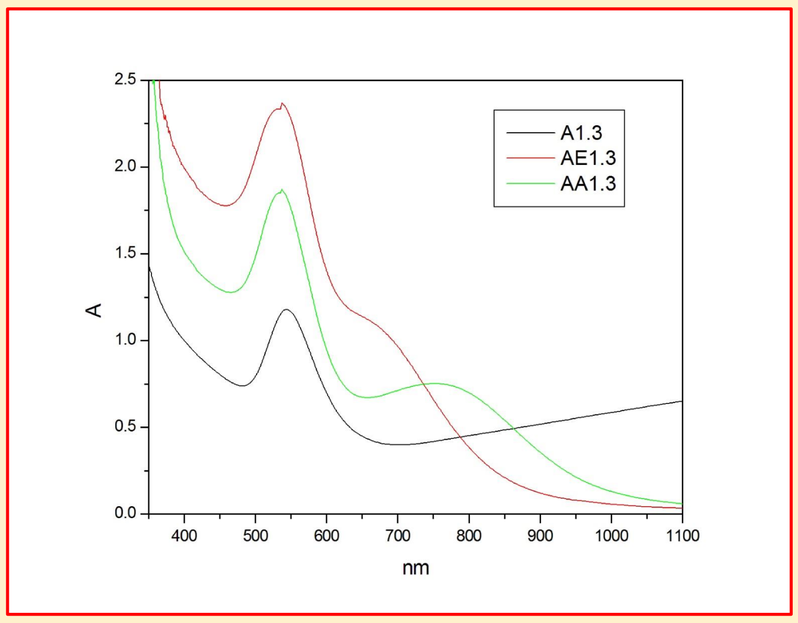

Figure 2. UV-Vis spectra of AuNPs solutions prepared by reaction of $HAuCl_4$ with *Melissa officinalis* L. extracts obtained using different solvents:
A – water;
AE – 70% ethanol;
AA – 70% acetone.

In case of aqueous extract, we assume the formation of large NPs with SPR peak at >1100 nm. The SPR peaks for extracts prepared using ethanol and acetone were observed at 680 and 780 nm, respectively. The shape of AuNPs also depends from extract to Au^{3+} ratio (Fig. 3). We observed that formation of non-spherical AuNPs is preferable at higher contents of Au^{3+} in reaction mixture.
TEM images confirms the formation both spherical and non spherical AuNPs (Fig. 4). We observed mainly triangles and large hexagons with size varied from 35 to 150 nm.

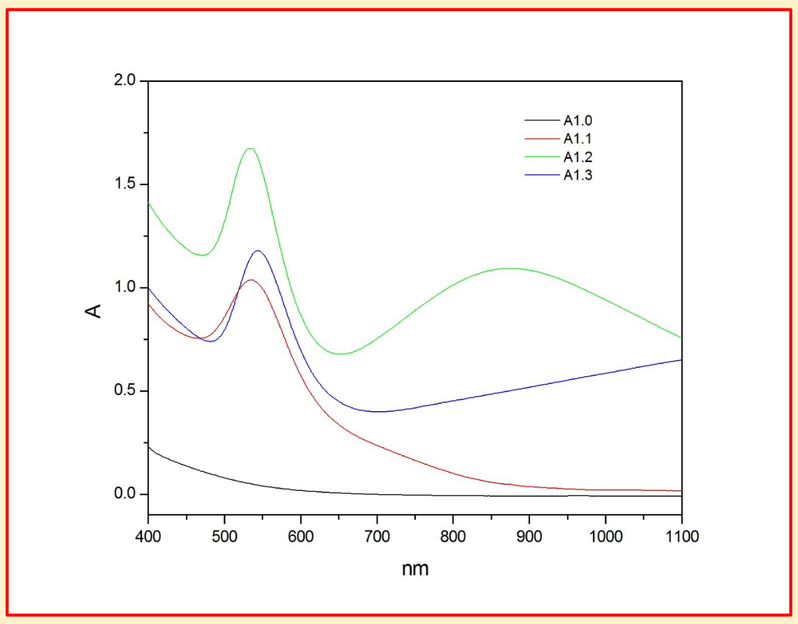

Figure 3. UV-Vis spectra of Au nanocolloid solutions prepared by reaction of *Melissa officinalis* L. extract (1 mg/ml) with different concentration of $HAuCl_4$:
A1.0 – 0 mM;
A1.1 – 0.25 mM;
A1.2 - 0.50 mM;
A1.3 - 0.75 mM.

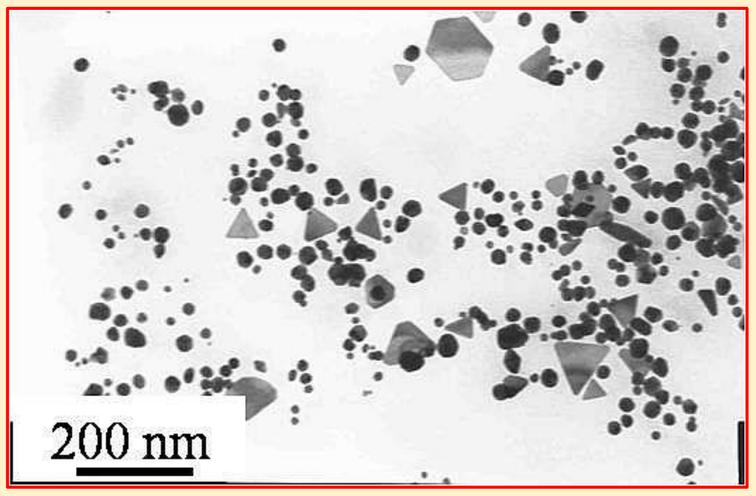

Figure 4. TEM images of AuNPs prepared by reaction of *Melissa officinalis* L.

Conclusions. In present study we have considered the possibility to use of the plants of mint family (Lamiaceae) for development of the green protocol for the synthesis of non-spherical AuNPs. The obtained results have shown that properties of AuNPs depends from the method of extracts preparation. At certain conditions, the triangle-and hexagon-shaped AuNPs with a size up to 250 nm can be prepared.

References

[1] Mariychuk R., Fejer J., Porubska J., Grishchenko L.M., Lisnyak V.V. (2019) *Appl. Nanosci*. DOI: 10.1007/s13204-019-00990-x
[2] Mariychuk R., Yakovlieva V., Porubska J., Eliasova A., Lisnyak V.V. (2019) *Proc. Int. Council Env. Eng. Edu. – Tech. Env. Protection (ICTEP 2019). IEEExplore*. art. no. 8968965,-P.177-180. DOI: 10.1109/ICTEP48662.2019.8968965
[3] Dzimitrowicz, A., Jamróz, P., diCenzo, *et al.* (2019) Arab. J. Chem., 12(8), P. 4118-4130. DOI: 10.1016/j.arabjc.2016.04.004
[4] Fierascu, I., Georgiev, M.I., Ortan, A. *et al*. (2017) Sci. Rep., 7 (1), art. no. 12428. DOI: 10.1038/s41598-017-12804-7