OPTOELECTRONICS AND ADVANCED MATERIALS RAPID COMMUNICATIONS Vol. 4, No. 9, September 2010, p. 1297 - 1300

Noble metals nanoparticles synthesis in plant extracts

R. C. FIERASCU[a,b,*], R. M. ION[a,b], I. DUMITRIU[a,b]
[a]*National Research & Development Institute for Chemistry and Petrochemistry – ICECHIM Bucharest, Romania*
[b]*Valahia University of Targoviste, Romania*

The noble metal nanoparticles, for example gold and silver nanoparticles, absorb strongly in the visible and near-infrared region when the frequency of an electromagnetic field becomes resonant with the surface plasmon coherent electron oscillation within the nanoparticles. Nowadays nanoparticles are widely used in photodynamic therapy (PDT) for treating cancer in vivo. The experiments regarding nanoparticle synthesis were conducted in plant extracts (Azadirachta indica, Anethum graveolens and Salvia officinalis).

(Received March 9, 2010; accepted September 15, 2010)

Keywords: Nanoparticles, Plant extracts, Synthesis, Characterisation

1. Introduction

Nanomaterials often show unique and considerably changed physical, chemical and biological properties compared to their macro scaled counterparts [1,2]. Synthesis of noble metal nanoparticles for applications such as catalysis, electronics, optics, environmental, and biotechnology is an area of constant interest [3–9]. Gold, silver, and copper have been used mostly for the synthesis of stable dispersions of nanoparticles, which are useful in areas such as photography, catalysis, biological labelling, photonics, optoelectronics and surface-enhanced Raman scattering (SERS) detection [10, 11].

Additionally, metal nanoparticles have a surface plasmon resonance absorption in the UV–Visible region. The surface plasmon band arises from the coherent existence of free electrons in the conduction band due to the small particle size [12, 13]. The band shift is dependent on the particle size, chemical surrounding, adsorbed species on the surface, and dielectric constant [14, 15].

Moreover, functionalized, biocompatible and inert nanomaterials have potential applications in cancer diagnosis and therapy [16–20]. The target delivery of anticancer drugs has been done using nanomaterials [16]. With the use of fluorescent and magnetic nanocrystals, the detection and monitoring of tumour biomarkers have been demonstrated [17, 18].

Gold and silver belong to a family of “free” electron metals that have a filled valence shell but an unfilled conduction band. When nanoparticles of these metals are irradiated with incident light, the "free" electrons move under the influence of the electromagnetic field and are displaced relative to their positive core, which creates an oscillating dipole. Oscillating dipoles absorb maximum energy at their resonance frequency, which lies in the visible range of the electromagnetic spectrum for gold and silver nanoparticles.

Generally, metal nanoparticles can be prepared and stabilized by physical and chemical methods; the chemical approach, such as chemical reduction, electrochemical techniques, and photochemical reduction is most widely used [21, 22]. Studies have shown that the size, morphology, stability and properties (chemical and physical) of the metal nanoparticles are strongly influenced by the experimental conditions, the kinetics of interaction of metal ions with reducing agents, and adsorption processes of stabilizing agent with metal nanoparticles [14, 15].

In order to be ready for use in biological systems, the nanoparticles must be synthesised trough “green” routes.

The green synthesis of nanoparticles involves three main steps, which must be evaluated based on green chemistry perspectives, including (1) selection of solvent medium, (2) selection of environmentally benign reducing agent, and (3) selection of nontoxic substances for the NPs synthesis [1, 22].

2. Experimental

2.1 Materials and methods

To achieve a “green” synthesis of the nanomaterials, reaction medium chosen was distilled water. The reducing agents used were plant extracts.

The reagents used for the synthesis ($HAuCl_4$, $AgNO_3$) were analytical grade and commercially available (Merck). The reagents chosen do not involves a toxic hazard on the environment.

The plants used were *azadirachta indica* – neem, *Anethum graveolens* – dill and *Salvia officinalis* – common sage.

The characterisation was performed using UV-Vis spectroscopy (SPECORD M400 Carl Jeiss Jena double beam spectrophotometer, equipped with a diffuse reflectance devices and connected to microprocessor), X-ray diffraction (DRON 2 X-ray diffractometer with Cu Ka radiation (λ = 0.154056 nm) and transmission electron microscopy (JEOL 2000 FX microscope).

2.2 Nanoparticle synthesis

The procedures for the natural extracts are similar, using plant leaves (for neem and dill) respectively sage leaves and flowers. The parts of the plants that were to be used were thoroughly washed, finely cut and then boiled in distilled water. Ultrasonication can also be used.

For the neem extract 10 g of neem leaves were extracted in 50 ml of distilled water.

From the extract obtained 2 ml were collected and divided into two flasks, in order to obtain 2 samples, each containing 2 ml of extract. In the two flasks, $AgNO_3$ and respectively $HAuCl_4$ of 10^{-3}M concentration were added, thus obtaining Samples I.1 and I.2.

The dill extract was realised similar to neem, using 20 g of dill in100 ml distilled water, finally obtaining samples II.1 and II.2.

The common sage extracts were obtained from 15 g of leaves (in 500 ml of distilled water) and 7 g of flowers (in 250 ml of distilled water).

From each extract, 4 samples were realised, each containing 20 ml of extract, named samples III.1 to III.4 for leaves, respectively IV.1 to IV.4 for flowers.

In samples III.1, III.3, IV.1 and IV.3, 20 ml of silver nitrate (10^{-3}M) were added. In samples III.2, III.4, IV.2 and IV.4 20 ml of $HAuCl_4$ solution (10^{-3}M) were added. In order to study the influence of light on the formation of the nanoparticles, samples III.1, III.2, IV.1 and IV.2 were kept under direct sunlight, while samples III.3, III.4, IV.3 and IV.4 were kept in the dark.

The appearance of the nanoparticles could be easily visually observed. The silver nanoparticle synthesis is indicated by the apparition of a specific colour varying from orange/green to pale yellow. The gold nanoparticles are signalled by a pale-red colour.

3. Results

3.1 Synthesis in neem extract

The synthesis of AuNP in neem extract was successful, confirmed by the fact that monometallic Au exhibits a well-defined absorption peak at aprox. 525 nm, which is the absorption band spectra of nanometer-size metallic gold particles (Fig. 1). However, the formation of silver nanoparticles was unsuccessful. Probably reason will be discussed in the Disscution chapter.

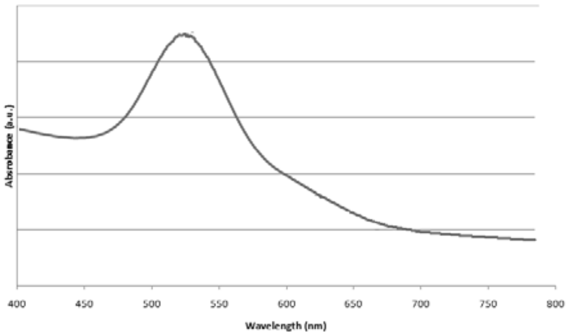

Fig. 1. UV-Vis spectra of sample I.2. It clearly exibits specific UV-Vis band of Au nanoparticles.

The XRD results confirms the apparition of the gold nanoparticles.

3.2 Synhtesis in dill extract

In dill, the synthesis of gold and silver nanoparticles was succesful. The UV-Vis and XRD results confirms de aparition of nanoparticles. In Fig. 2 are presented the TEM images of gold (a) and silver nanoparticles obtained.

In both cases, the average size was about 10 nm.

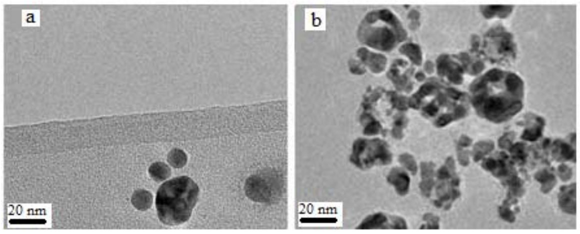

Fig. 2. TEM image of the synthesised nanoparticles. (a) sample II.1 – AgNP; (b) sample II.2 AuNP.

3.3 Synthesis in sage extracts

The synthesis of nanoparticles in sage extracts was conducted in order to study the influence of a very important parameter (sunlight) on the nanoparticle growth.

The synthesis was successful, confirmed by UV-Vis (Fig. 3), XRD (Fig. 4) and TEM results.

The difference between the working conditions lead to different results, that are to be discussed.

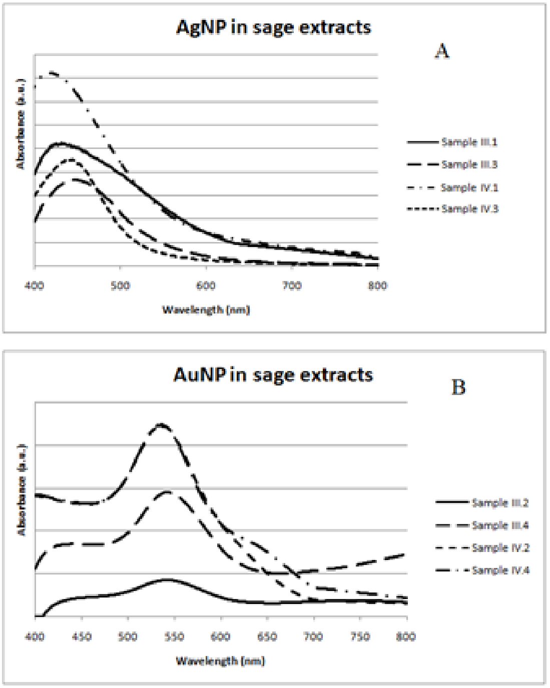

Fig. 3. UV-Vis results obtained for the synthesised nanoparticles. (A) Silver nanoparticles (obtained in leaves – samples III.1 and III.3 and flowers extract – samples IV.1 and IV.3, kept under direct sunlight – samples III.1 and IV.1 and kept in dark – samples III.3 and IV.3); (B) Gold nanoparticles (obtained in leaves – samples III.2 and III.4 and flowers extract – samples IV.2 and IV.4, kept under direct sunlight – samples III.2 and IV.2 and kept in dark – samples III.4 and IV.4).

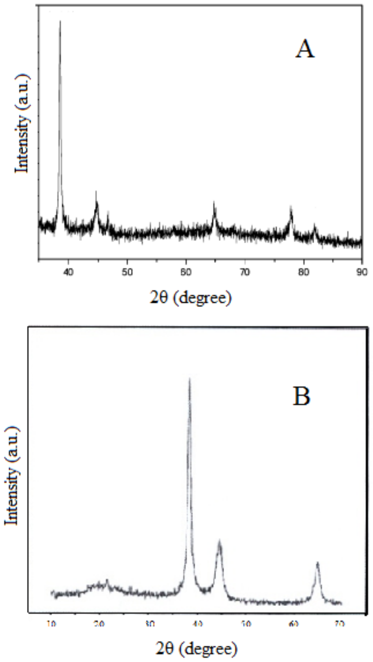

Fig. 4. XRD patterns obtained for (A) silver nanoparticles and (B) gold nanoparticles.

4. Discussions

The composition of the extracts is mentioned in the literature datas.

Neem extract should mainly consist of nimbin, nimbinin, nimbidin, azadirachtin and others [23]. Dill extract constituents are apiole, carvone, myristicin, umbelliferone and others [24], while sage extract could contain among others cineol, borneol, ursolic acid, favones, flavonoid glycosides and chlorogenic acid [25].

According to literature data [22] the effective reducing agents involved in the synthesis of the nanoparticles are the flavonoides and/or terpenoides .

Future studies regarding the compounds responsable of the nanoparticle growth will be conducted by our group.

The synthesis of silver nanoparticles in neem extract was unsuccesful. This indicates that the active constituents of the neem extracts are not powerfull enough reducing agents, unlike the extracts obtained from dill and sage.

The experiments regarding nanoparticle synthesis in sage extracts (leaves and flowers) allow to draw some conclusion.

The exposure to direct sunlight clearly influences the nanoparticle synthesis. Best results in obtaining silver nanoparticles were for sample IV.1, followed by sample III.1. Also, the results obtained for sample IV.3 are better than those for sample III.3.

This means that the flower extract is a more powerful reducing agent than the leave extract for the synthesis of silver nanoparticles. Also, the synthesis is dependent to the presence of light (better results for samples III.1 and IV.1 than those for samples III.3 respectively IV.3).

Considering both parameters, it can be seen that the sample obtained from flower extract and kept under sunlight (IV.1) offers much better results than that obtained from leaves extract and kept in the dark (III.3). The results obtained for sample III.1 (sample in leaves extract and irradiated with direct sunlight) are better than those for sample IV.3 (sample in flower extract and kept in the dark).

In conclusion the best parameters to be used for the synthesis are flower extract and exposure to direct sunlight.

Regarding the synthesis of gold nanoparticles, it can be observed that in this case also the flower extract is a much better reducing agent than the leaves extract. In this case, both samples obtained in flower extract (series IV) shows better results than those in leave extract (series III). In the case of a weaker reducing agent (leave extract), the sunlight becomes a very important parameter (it is a big difference between samples III.4 and III.2). Surprisingly, the absence of light (III.4) offers better results than its presence (III.2).

For the samples obtained in flower extract, the UV-Vis peaks are practically identical, so the influence of light is negligible.

In conclusion the parameter that must be obeyed is the presence of sage flower extract.

5. Conclusions

Some easy and reproductable ways for the synthesis on noble metal nanoparticles were presented.

The use of natural extracts, distilled water and practically nontoxic reagents allows the synthesis pathways presented to be considered “green”, and so permeating the synthesised nanoparticles to be used in sensitive areas such as biomedicine.

The present study will be continued in order to establish the reaction mechanism and to perform more quantitative studies.

References

[1] P. Raveendran, J. Fu, S. L. Wallen, J. Am. Chem. Soc. **125**, 13940 (2003).
[2] L. Li, J. Hu, A. P. Alivistos Nano Lett. **1**, 349 (2001).
[3] I. Hussain, M. Brus, A. J. Papworth, A. I. Cooper, Langmuir, **19**, 4831 (2003).
[4] D. J. Burleson, M. D. Driessen, R. L. Penn, J. Environ. Sci. Health A **39**, 2707 (2005).
[5] M. D. Cheng, J. Environ. Sci. Health A **39**, 2691 (2005).
[6] S. O. Obare, G. J. Meyer, J. Environ. Sci. Health A **39**, 2549 (2005).
[7] G. Yuan, J. Environ. Sci. Health A **39**, 2545 (2005).
[8] T. Masciangioli, W. X. Zhang, Environ. Sci. Technol. **37**, 102A–8A (2003).
[9] M. A. Albrecht, C. W. Evans, C. L. Raston. Green Chem. **8**, 417 (2006).
[10] A. M. Smith, H. Duan, M. N. Rhyner, G. Ruan, S. A. Nie. Phys. Chem. Chem. Phys. **8**, 3895 (2006).
[11] G. J. Kearns, E. W. Foster, J. E. Hutchison. Anal Chem. **78**, 298 (2006).
[12] C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed. Chem. Rev. **105**, 1025 (2005).
[13] P. M. Tessier, O. D. Velev, A. T. Kalambur, J. F. Rabolt, A. M. Lenhoff, E. W. Kaler. J. Am. Chem. Soc. **122**, 9554 (2000).
[14] P. Mulvaney. Langmuir, **12**, 788 (1996).
[15] B. Knoll, F. Keilmann. Nature **399**, 134 (1999).
[16] S. Sengupta, D. Eavarone, I. Capila, G. L. Zhao, N. Watson, T. Kiziltepe. Nature, **436**, 568 (2005).
[17] I. Brigger, C. Dubernet, P. Couvreur, Adv. Drug Deliv. Rev. **54**, 6310 (2004).
[18] P. Alivisatos, Nat. Biotechnol. **22**, 47 (2004).
[19] X. H. Gao, Y. Y. Cui, R. M. Levenson, L. W. K. Chung, S. M. Nie, Nat. Biotechnol. **22**, 969 (2004).
[20] M. Singh, S. Singh, S. Prasad, I. S. Gambhir, J. Dig. Nanomater. Biostruct. **3**, 115 (2008).
[21] K. V. Sharma, R. A. Yngard, Y. Lin Advances in Colloid and Interface Science **145**, 83 (2009).
[22] J. L. Gardea-Torresdey, J. R. Peralta-Videa, J. G. Parsons, N. S. Mokgalaka, G. la Rosa, Met. Nanocl. Cat. Mat. Sci., 401 (2008).
[23] S. Akhondzadeh, M. Noroozian, M. Mohammadi, S. Ohadinia, A. H. Jamshidi, M. Khani, J. Clin. Pharm. Ther., **28**(1), 53 (2003).
[24] S. Ganguli, Curr. Sci., **82**(11), 1304 (2002).
[25] I. Blank, W Grosch, J. Food Sci. **56**(1), 63 (1991).

---

*Corresponding author: radu_claudiu_fierascu@yahoo.com