Gold nanoparticles green synthesis with clove oil: Spectroscopic and theoretical study

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Introduction / Objectives / Aims

The development of new green methods for the synthesis of metal nanoparticles (NPs) is a fast developing trend in modern nano-science [1]. From an ecological point of view, it is better to minimize the use of organic solvents and chemical reagents for dispersion and reduction in the synthesis of metal NPs. Currently, there is a trend question/problem/task in the green synthesis of metal NPs, and it is more and more developing by a researchers' community. Using biochemical pathways for preparation of metal NPs such as the use of plant extracts as reductant and surfactant simultaneously. For example, black tea leaf [2], *Erythrina indica* root [3], *Nyctanthes arbortristis* flower [4]. It was shown that natural components of the extracts, like polyphenols, flavonoids, and polysaccharides, are acted as reducing and dispersing agents for silver cations. From a theoretical point of view, plants' essential oils have much higher synthetic efficiency for metal NPs production. The studies on the use of essential oils as reducing and stabilizing agents for metal NPs production are known, however, these are relatively rare. Some essential oils are very rich for reducing agents, for example, Clove oil contains about 90% of eugenol – organic phenol with reductive properties. Moreover, most of the ingredients of essential oils are lipophilic are can envelop metal NPs surface and stabilize them.

In the present work, we have focused on the improvement of the synthesis of Au-NPs via the reaction of tetrachloroauric acid with the clove essential oil firstly described by Kaur et al [5], and on the theoretical explanation of the synthetic pathway and its mechanism in terms of the quantum chemical density functional theory (DFT) method. It must be mentioned that Milczarek and Ciszewski have studied the use of pure eugenol for the synthesis of gold NPs [6].

Methods

1) Investigation of the reaction between tetrachloroauric acid and clove essential oil in a water-organic solvent medium.
2) Using of UV-VIS methods for kinetic analysis.
3) Analysis of products of oxidation of essential oils' components. Interpretation of experimental data of FT-IR spectrometry and GC/HPLC for understanding the mechanism of redox reaction that takes place in considered synthesis.
4) Optimization of Au-NPs sample preparation.
5) Quantum chemical modeling of the mechanism.

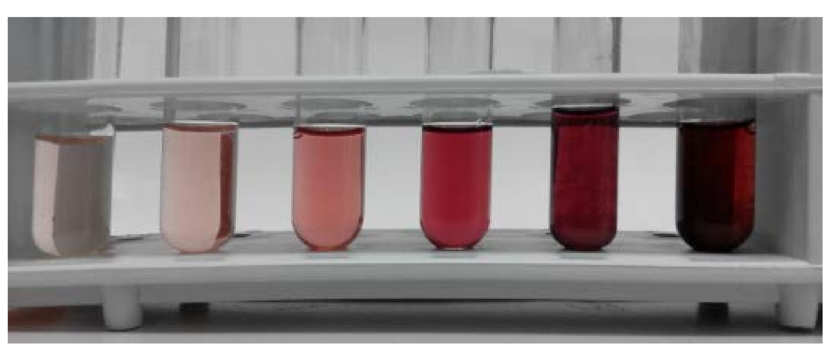

Figure 1. Six samples of prepared gold nanoparticles with different starting concentrations of tetrachloroauric acid, from left to the right (mmol/L): 0.02, 0.04, 0.10, 0.20, 0.30, 0.40.

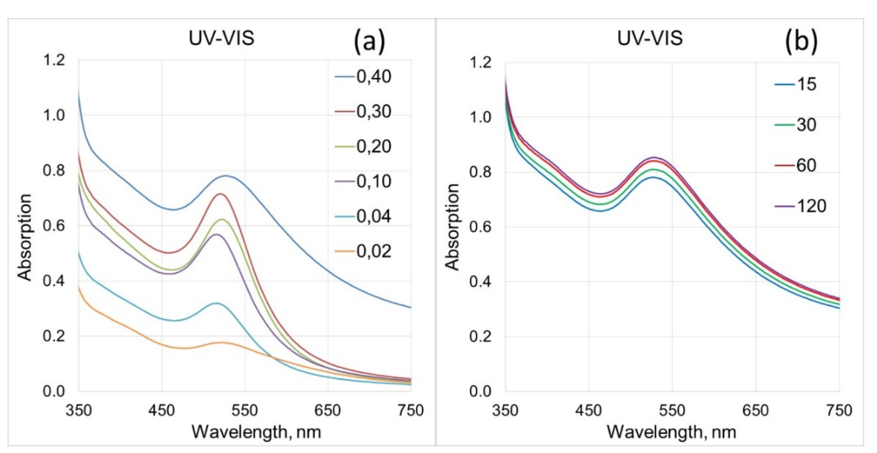

Figure 2. UV-VIS spectra of six solutions with different starting concentration (0.02, 0.04, 0.10, 0.20, 0.30, 0.40 mmol/L) of tetrachloroauric acid (a); Kinetic study (15, 30, 60 and 120 min) of formation of gold nanoparticles with 0.40 mmol/L starting concentration of $HAuCl_4$ (b).

Results

As the main natural reducing and stabilization agent we have decided to use clove essential oil. The choice is dictated by numerous successful protocols described in modern papers. It was shown that the main component of clove essential oil – eugenol, can act as an appropriate reducing agent due to its phenolic structure. Moreover, the oil is relatively cheap due to its high concentration in a clove raw stuff and it is not harmful to human, what is established during long used in medicine.

Varying the experimental conditions, we have succeed in developing new simple methods for the synthesis of Au-NPs with using of nontoxic reagents like sodium hydroxide diluted solution, tetrachloroauric acid – the source of gold, clove essential oil and its main component eugenol as reducing and stabilization agent. The photo of the about described six parallel experiments presented in Figure 1. The clear pinkish solutions indicate the formation of desired Au-NPs.

Corresponding UV-VIS spectra presented in Figure 2. Relatively high baseline in the case of Fig.2a for 0.40 mmol/L concentration and in the case of Fig.2b can be explained by partial precipitation in the reaction mixture, which testifies that the concentration of 0.40 mmol/L is too high, and maximal appropriate concentration must about 0.30 mmol/L. According to Fig.2b, the difference between spectrum after 1 hour and 2 hours is quite small, which testifies that 2 hours is totally enough for the reaction completeness. The absorption maxima are in the range of 520-530 nm, which correspond to the formation of classical spherical gold nanoparticles. Absorption at the lower wavelength range of 320-380 nm corresponds to the absorption of eugenolate anion itself, that is present in basic solution of eugenol.

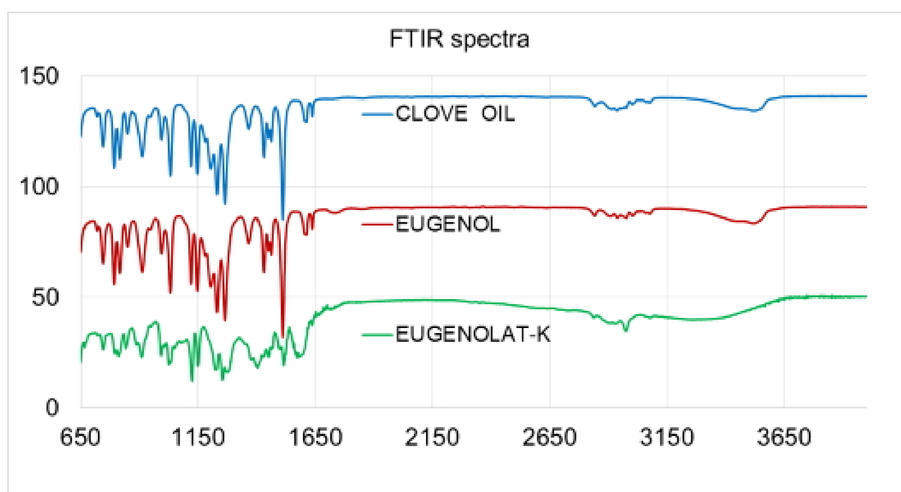

Figure 3. FTIR spectra of the clove essential oil, extracted eugenol, and potassium eugenolate.

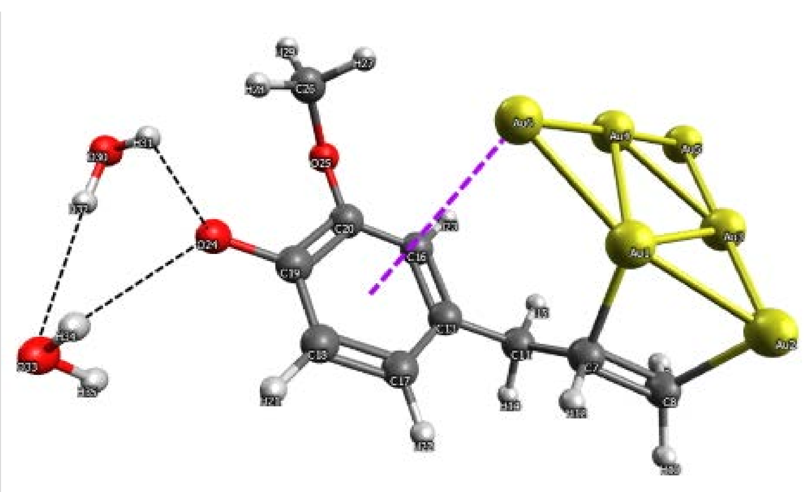

Figure 4. Modelled interactions of eugenolate anion with Au6 cluster and with two water molecules.

Conclusions

It was determined that the terminal double bond of the allylic fragment in the eugenol molecule has the key role in stabilization of gold nanoparticles. Thus, exactly this C7-C8 ethenyl group forms a strong bond with gold atoms on the surface of the nanoparticle (modelled as Au_6 cluster), whereas the other-side phenolic group, which is in an anionic form (the O24 atom) in basic solution, strongly interacts with water molecules and forced the gold-eugenol system to be stable instead of conglomeration to bulk gold particles.

References

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