engineering proceedings

MDPI

Proceeding Paper

Effect of Glutathione on the Destruction Kinetics of Silver Nanoparticles in Aqueous Solutions: An Optical Study Under Neutral And Alkaline Conditions [†]

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[†] Presented at the 10th International Electronic Conference on Sensors and Applications (ECSA-10), 15–11 30 November 2023; Available online: https://ecsa-10.sciforum.net/.

Abstract: The interaction of nanostructured metal particles with the molecular components of biosystems differ significantly from the processes that take place in the presence of ions of the same metals. This unequivocally indicates the need to take into account not only the course of chemical processes, but also implies to discuss certain physical effects that are usually neglected when considering such interactions. In this work; we studied the interaction of silver nanoparticles dispersion (Ag-NP) in ethylene glycol with particle size less than 100 nm (Sigma-Aldrich 658804) with glutathione in an water and carbonate buffer (pH 10). The choice of glutathione (GSH) is due to the fact that it plays a significant role in intracellular processes; participating in the protection of intracellular components from the toxic effects of heavy metal ions; at the same time; differences in its interaction with silver ions and nanoparticles were experimentally demonstrated. A series of optical studies of the absorption and emission spectra of solutions of silver nanoparticles with GSH was carried out in order to establish the dominant processes in the system. It was shown that the above mentioned silver nanoparticles in aqueous solutions spontaneously decompose over time, while glutathione differently affects these processes in water and carbonate buffer. It was shown that not only the local surface plasmon resonance bands, but also the emission spectra of Ag-NP~GSH solutions in the region of 350-550 nm change with time. The sources of such radiation can be carbon quantum dots (CQD), which, according to published data, can be formed during the synthesis of silver nanoparticles and effectively luminesce in this region of the spectrum. Raman spectroscopy data confirm the presence of CQD in the used dispersion nanoparticles of silver. The presence of quantum dots in the system makes it possible to indirectly track the presence of silver nanoparticles, which are booster centers, enhancing the emission of CQDs.

The studies allow us to state that the interaction of glutathione with silver nanoparticles is a complex topochemical process in which, in addition to chemical reactions, the processes of transformation of silver nanoparticles and changes in the distribution of their sizes and chemical/physical functionality take place.

Keywords: glutathione; silver nanoparticles; carbon quantum dots; plasmon, luminiscence

Citation: To be added by editorial staff during production.

Academic Editor: Firstname Lastname

Published: 15 November 2023

1. Introduction

Glutathione is a major endogenous antioxidant that protects cells against oxidative stress through its ability to bind to and reduce ROS. The production of free radicals induced by nanoparticles leads to a reduction of GSH to oxidized form, followed by induction of oxidative stress [1]. Thus, preservation of the GSH-mediated antioxidant defense system is critical for cell survival. However, various studies have indicated that cellular levels of GSH are either increased or decreased after in vitro treatment with AgNPs [2].

The increased levels of GSH observed in some AgNP-treated cells [3] may involve cellular responses for coping with AgNP-mediated oxidative damage. By contrast, the decreased levels of GSH noted in AgNP-treated human skin carcinoma and fibrosarcoma cells [4] suggest an inhibition of GSH-synthesizing enzymes and/or abnormally increased demand for GSH in conjugation with electrophilic molecules

The interaction of nanostructured metal particles with the molecular components of biosystems differ significantly from the processes that take place in the presence of ions of the same metals [5]. This unequivocally indicates the need to take into account not only the course of chemical processes, but also implies to discuss certain physical effects that are usually neglected when considering such interactions.

In this work, we studied the interaction of silver nanoparticles dispersion (Ag-NP) in ethylene glycol with particle size less than 100 nm (Sigma-Aldrich 658804) with glutathione in an water and carbonate buffer (pH 10). The choice of glutathione as was described above is due to the fact that GSH plays a significant role in intracellular processes, participating in the protection of intracellular components from the toxic effects of heavy metal ions; at the same time, differences in its interaction with silver ions and nanoparticles were experimentally demonstrated. The thiol group of glutathione has been shown to form an extremely strong bond with the silver [6].

It was shown that silver nitrate significantly affects the quantity of glutathione in the blood plasma by oxidizing the reduced glutathione to disulfide 2 GSH <=> -GSSG- 2H+) or the formation of the Ag-SG complex, which also indicates the protective role of glutathione, thus neutralizing the toxic effect silver [7]. As for Ag NP, it was demonstrated, that cytotoxity induced by them was even higher compared than that observed when AgNO3 was used as a silver ion source. Namely Ag NPs induce reactive oxygen species (ROS) generation [8] (which play important roles in a variety of normal biochemical functions, but abnormality in their functions results in pathological processes, for example, inducing apoptosis [9]), and suppression of reduced glutathione in human Chang liver cells. ROS generated by AgNPs resulted in damage to various cellular components, DNA breaks, lipid membrane peroxidation, and protein carbonylation [10]).

In this work, a series of optical and luminescence studies in the absorption and emission spectra of aqueous silver nanoparticles solutions with GSH was carried out. The obtained results were shown that the AgNPs spontaneously decompose over time in aqueous solutions with different mechanism in water and carbonate buffer, when the glutathione was added to the solution.

2. Materials and Methods

AgNPs (<100 nm, 10% wt) in ethylene glycol, Glutathione (99%), Sodium carbonate (>99, 5%), and Sodium bicarbonate (>99, 7%) were received from Sigma-Aldrich. The optical absorbance was studied by UV-Vis spectroscopy on Umico SQ2800 (UNICO, Dayton, NJ, USA). Luminescence spectra were measured using spectrometer USB2000+ (OCEAN OPTICS INC, Dunedin, FL, USA).

3. Results and Discussion

A 0.01 M carbonate buffer solution (pH~10) was used to prepare the AgNPs buffer solution and the GT one. First, a 5 mM AgNPs buffer solution was prepared by mixing the initial AgNPs (10% wt) in ethylene glycol with carbonate buffer solution in terms of the silver amount. Then, GT solution was prepared in carbonate buffer at concentrations of 20 mM. The AgNPs buffer solution and the GT one were mixed in equal volumes [11]. Analogously, the AgNPs solution in water was prepared and 20 mM GT water solution in equal volumes was added to the AgNPs solution. The absorbance spectra of the prepared solutions were measured in 00, 10, 20, 30, 40, 50 min, 1, 1:30, 2, 2:30, 3, 3:30, 4 hours and 2 days after mixing, while the luminescence spectra of ones were measured in 30 min and 1 hour.

UV-Vis spectra showed that Ag plasmon peak maximum was characterized by different behavior in the water and the buffer solution of AgNPs after adding the GT (Figure 1a and Figure.2a).

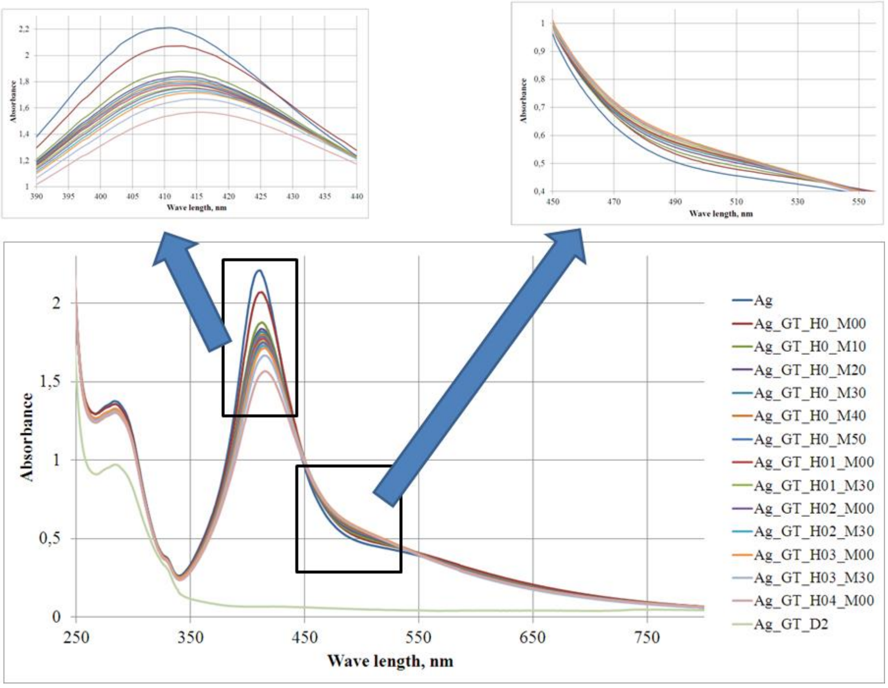

Figure 1. a. UV-Vis spectra of the water solution of AgNPs after adding the GT.

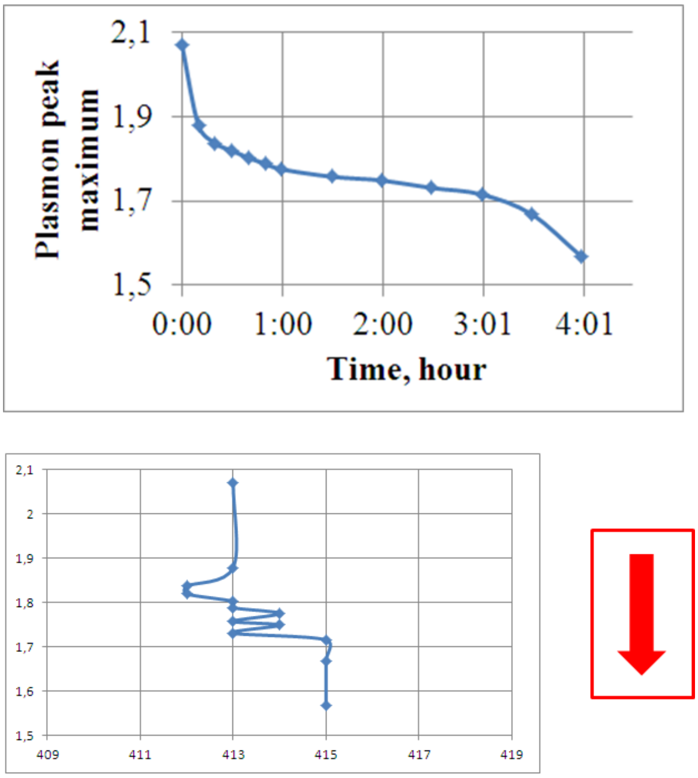

Figure 1. b. Dynamics behavior of the plasmon peak maximum in the water solution of AgNPs after adding the GT.

In Figure 2a and 2 b is shown the change dynamics of the plasmon peak maximum in both the water solution of AgNPs and the buffer one. The plasmonic band intensity at

413 nm decreased with slight bathochromic shift in maximum was found in the water solution of AgNPs along with decreasing the plasmonic intensity at 520 nm which indicated the fast AgNPs dispergation (Figure.1a). Quite different process was observed in the buffer solution where in the beginning the decrease in the plasmon intensity at 415 nm occurred, and then its increasing followed by decreasing was observed. On the other hand, the plasmon band at 550 nm was increasing which indicated the occurrence of AgNPs agglomeration in the first stage.

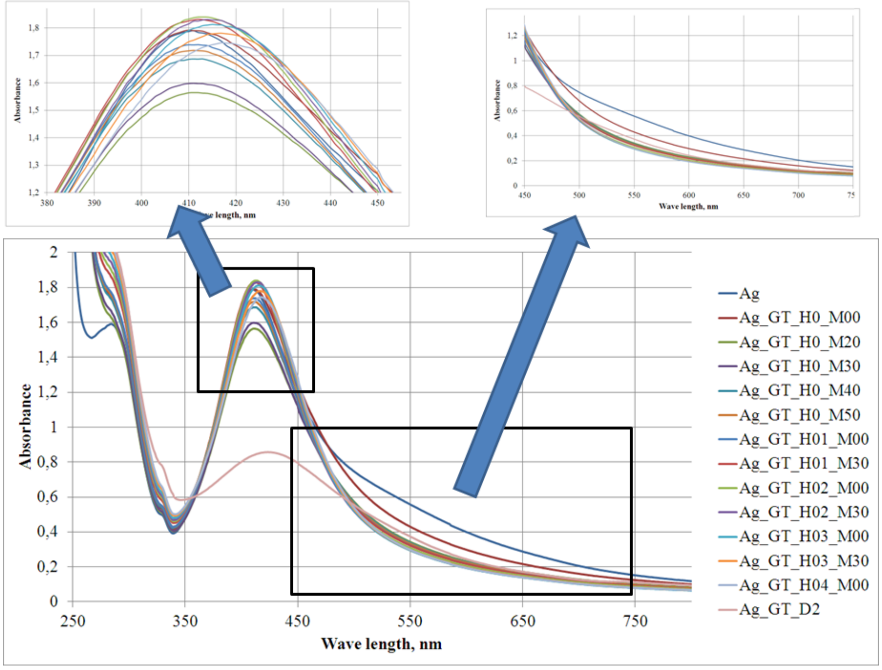

Figure 2. a. UV-Vis spectra of the buffer solution solution of AgNPs after adding the GT.

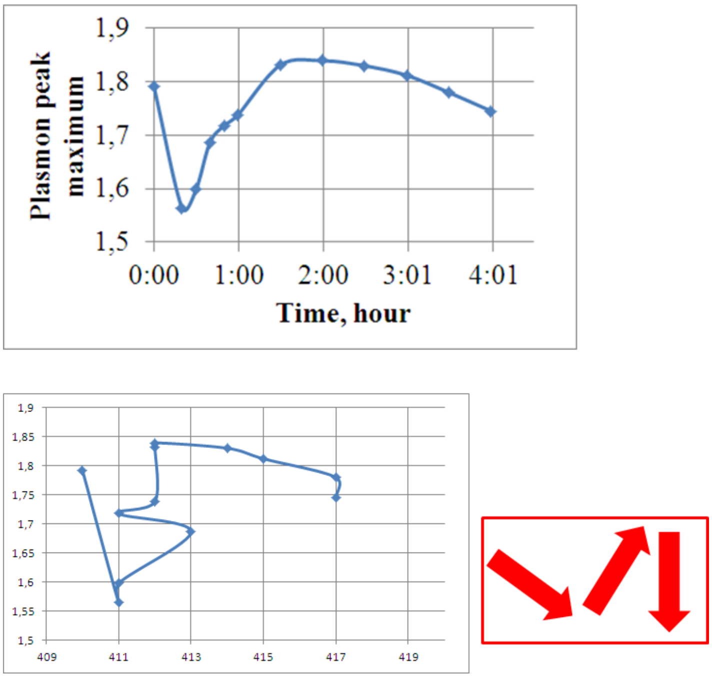

Figure 2. b. Dynamics behavior of the plasmon peak maximum in the buffer solution of AgNPs after adding the GT.

Also, the luminescence spectra relieved the different behavior in the watter and the buffer solution of AgNPs (Figure 3a and 3b).

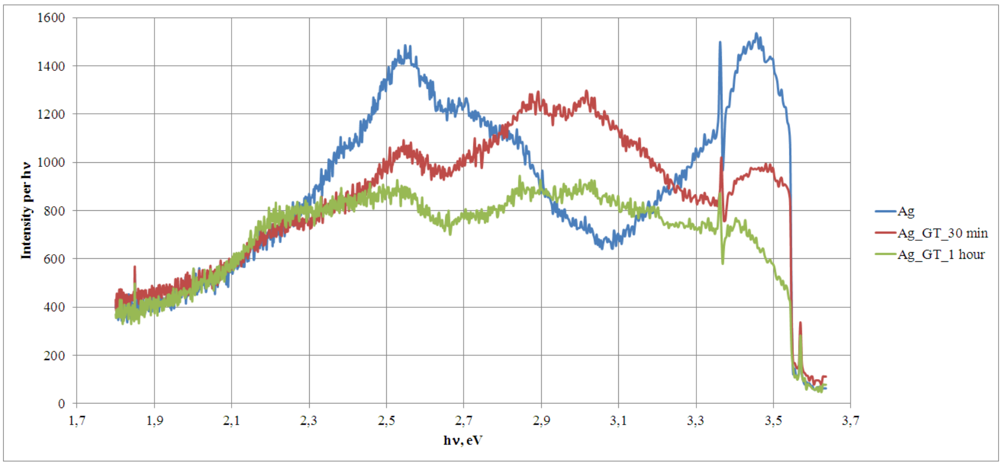

Figure 3. a. Luminescence spectra of the water solution of AgNPs after adding the GT.

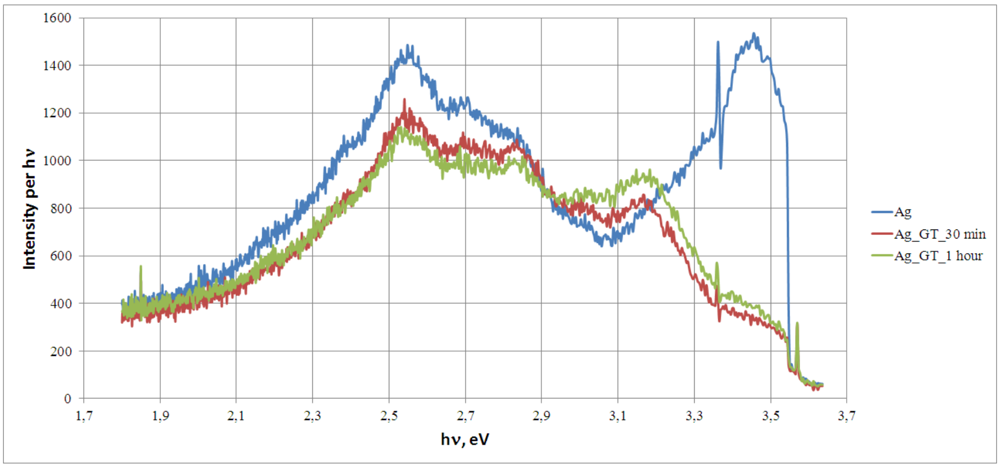

Figure 3. b. Luminescence spectra of the buffer solution of AgNPs after adding the GT.

The spectra of the initial both water and buffer AgNPs solution were characterized with the presence of two wide bands at 3.4 and 2.52 eV. The sources of such radiation can be carbon quantum dots (CQD), which, can be formed during the AgNPs preparation and effectively luminesced in this region of the spectra [12-14]. Raman spectroscopy data confirm the presence of CQD in the used dispersion nanoparticles of silver [11]. The AgNPs defragmentation in the water and buffer solution resulted in the luminescence band diminish at 3.4 and 2.52 eV. It is interesting to notice the appearance of the new luminescence band at 2.9 eV diminished during the time in the water AgNPs solution (Figure 3a)

So, the presence of quantum dots in the solution makes it possible to indirectly track the presence of silver nanoparticles, which are booster centers, enhancing the emission of CQDs.

4. Conclusions

The studies allow us to state that the interaction of glutathione with silver nanoparticles is a complex topochemical process in which, in addition to chemical reactions, the processes of transformation of silver nanoparticles and changes in the distribution of their sizes and chemical/physical functionality take place.

Author Contributions: Conceptualization, B.S. and S.K; methodology, E.M.; software, P.B.; validation, E.M., S.K. and P.B.; formal analysis, S.K.; investigation, E.M.; resources, B.S.; data curation, P.B.; writing—original draft preparation, S.K.; writing—review and editing, P.B.; visualization, S.K.; supervision, B.S.; project administration, E.M.; funding acquisition, B.S. All authors have read and agreed to the published version of the manuscript.”.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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