

THE INFLUENCE OF REDOX CHEMICAL SURFACE TREATMENTS ON SILVER NANOPARTICLES

M. TUDOSE^{a*}, C. MUNTEANU^a, G. MARINESCU^a, D. CULITA^a, P. IONITA^{a,b}

^a*Institute of Physical Chemistry, 202 Spl. Independentei, Bucharest, Romania*

^b*University of Bucharest, Organic Chemistry, Biochemistry and Catalysis Department, 90–92 Panduri, Bucharest, Romania*

Silver nanoparticles are prepared by a chemical reduction method, using silver nitrate as the metal precursor and sodium borohydride as the reducing agent. Polyvinylpyrrolidone and 1,2-dimethoxy-ethane are used as stabilizing ligands on the surface nanoparticles. The silver nanoparticles obtained with this method are shown to exhibit typical surface plasmon absorption behavior at about 400 nm, and transmission electron microscopy and dynamic light scattering show that the average size of silver nanoparticles is between 30–50 nm, depending on the chemical procedure and the stabilizer used. The effect of hydrogen peroxide as the oxidant and hydrazine as the reducing agent is studied in conjunction with methylene blue dye. It is demonstrated that the chemical surface modification has great influence on silver nanoparticle reactivity.

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1. Introduction

The field of nanoscience has blossomed over the last 20 years because of the demand for miniaturization. As the role of nanotechnology increases, it also becomes increasingly important in many areas such as computing, sensors and biomedical applications. In recent years, noble metal nanoparticles have been the subject of focused research because many properties of nanoparticles (electronic, optical, mechanical, magnetic, and chemical) are significantly different from those of bulk materials [1,2].

The unique properties of nanoparticles are attributed mainly to their small size and large specific surface area and, therefore, can be said to arise from their high surface/volume ratio. Moreover, the quantum confinement of the electron-hole pairs in semiconductor nanoparticles, the surface plasmon resonance of some types of metal nanoparticles, and the super-paramagnetism of magnetic nanomaterials [3,4] contribute to their intensely studied properties. For these reasons, metallic nanoparticles are used in many applications in different science fields, such as catalysis, electronics, and photonics.

A variety of preparation routes for metallic nanoparticles have been reported [5,6], and notable examples include the reverse micelles process [7,8], salts reduction [9], microwave dielectric heating reduction [10], ultrasonic irradiation [11], radiolysis [12], solvothermal synthesis [13], and electrochemical synthesis [14,15].

The simplest and most commonly used bulk-solution synthetic method for metal nanoparticles is the chemical reduction of metal salts [16,17]. Production of nanosized metal silver nanoparticles with different morphologies and sizes [18] has been reported previously using chemical reduction of silver salts [19]. This synthetic method involves reduction of an ionic salt in an appropriate medium, usually in the presence of a surfactant, using various reducing agents [20].

*Corresponding author: madalina_tudose2000@yahoo.com

The silver nanoparticle dispersion emits an intense color due to plasmon resonance absorption. The free electrons on the surface of the metal are in the conduction band, so the surface plasmon resonance is therefore a collective excitation of the electrons in the conduction band. Electrons are limited to specific vibration modes by the particle sizes and shapes, so the metallic nanoparticles have characteristic optical absorptions in the UV–visible wavelength (UV–Vis) region [21].

In this work, we use an aqueous silver nitrate solution and sodium borohydride with the primary goal of obtaining, and subsequently characterizing, two types of silver nanoparticles (Ag NPs). Specifically, the two types of Ag NPs are those protected by polyvinylpyrrolidone (PVP) and those protected by 1,2-dimethoxy-ethane (DME). The secondary goal of the work is to study the reactivity of the synthesized Ag NPs after chemical surface modification by different reagents.

2. Experimental

2.1 Materials and Methods

Chemicals and materials were purchased from Sigma-Aldrich and Chimopar, and all chemicals were used as received. Doubly distilled water was used throughout all of the experiments. Ultraviolet–visible spectroscopy was performed at ambient temperatures in 1 cm path length quartz cells using a UVD-3500 double beam spectrophotometer. Transmission electron microscopy (TEM) was performed on an FEI Tecnai G2-F30 S-Twin field-emission gun scanning transmission electron microscope (FEG STEM). The TEM measurements were performed at 300 kV with a line-in-line resolution of 0.205 nm. To make the TEM samples, a drop of the silver nanoparticles suspension was mounted on a copper grid with a holey carbon film, and the solvent was allowed to evaporate at room temperature. The mean size of the nanoparticles was measured using a Beckman Coulter dynamic light scattering (DSL) apparatus.

2.2 Nanoparticles synthesis

For the preparation of Ag NPs, two stabilizing agents—polyvinylpyrrolidone (PVP) and 1,2-dimethoxy-ethane (DME) were used. A silver nitrate solution (from 0.001 M to 0.005 M) and sodium borohydride (from 0.002 M to 0.01 M) were used as a metal salt precursor and a reducing agent, respectively. A 0.3% stabilizing agent (PVP or DME) was required in both types of synthesis. A typical synthesis procedure included adding to 50 mL (0.01 M) of an ice-cold solution of sodium borohydride, while stirring, 3.3 mL (0.005 M) of silver nitrate and 1.66 mL (0.3%) of the protecting ligand. The final mixture was yellow to brown, depending upon the concentration of the starting materials.

2.3 Influence of hydrogen peroxide and hydrazine on Ag NPs reactivity towards methylene blue dye

To the previously synthesized Ag NPs was added a solution of methylene blue in water, and UV–Vis spectra was then recorded at specific intervals of time, usually 5 min, for up to 2 h or even 1–2 days. While studying the influence on the Ag NPs of hydrogen peroxide as an oxidant and hydrazine as a reducing agent, an additional water solution of these reactants was added and spectra were recorded using the same conditions.

3. Results and discussions

3.1 Synthesis of Ag NPs

The most versatile method by which nanoparticles are synthesized is via a reaction between a metallic salt and a chemical reducing agent. Among the variants of this method, it is worth mentioning the formation of nanoparticles using a soft reducing agent such as sodium

borohydride [22], and a well-known stabilizing agent such as PVP or DME. The formation of silver nanoparticles is subsequently confirmed by TEM and DLS, and Fig. 1 shows a typical TEM image of such nanoparticles. The DLS analysis shows that Ag NPs protected by PVP have an average size of 30 nm with a polydispersity index of 0.44, while DME-protected Ag NPs have an average size of 48 nm with a polydispersity index of 0.48. The IR spectra of solid Ag NPs are shown in the Supplementary material.

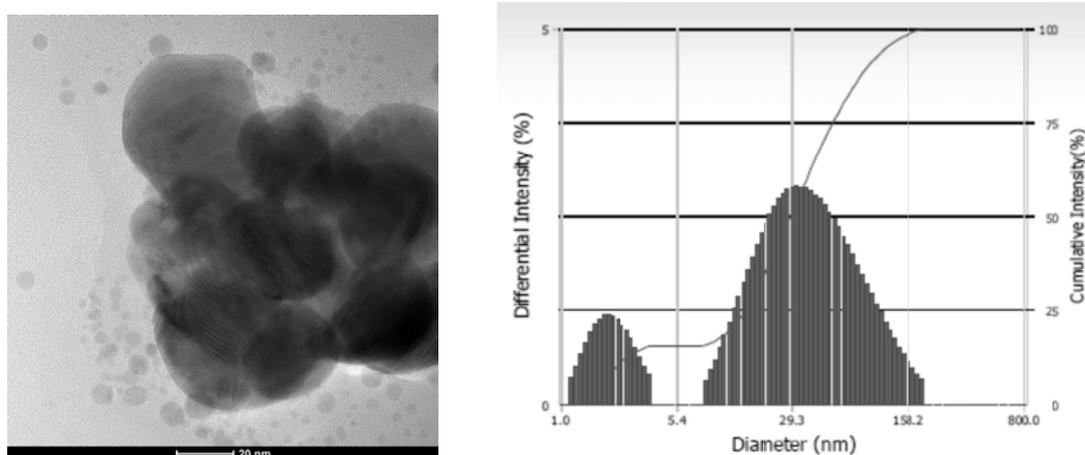


Fig. 1. TEM micrograph of the synthesized silver nanoparticles and the corresponding DLS measurement

Spectroscopy in the ultraviolet and visible wavelengths is one of the most widely used techniques for structural characterization of metallic nanoparticles. The pale yellow-brown silver colloids prepared by this method exhibit a surface plasmon absorption band at around 400 nm, which shows highly intense absorption values (Fig. 2).

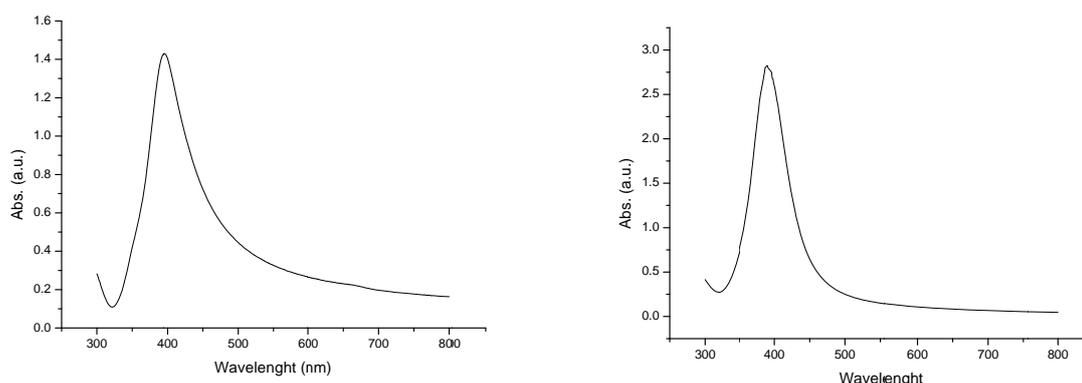


Fig. 2. UV-Vis spectra of Ag NPs obtained using PVP (left) and DME (right) as stabilizers

Our experiments show that all the nanoparticles are quite stable when kept at room temperature and in the dark, but after several days a small change in the UV-Vis spectra of these nanoparticles can be noticed. Starting with measurements taken a day after their synthesis, the Ag NPs plasmon absorption bands show a small bathochromic shift, which can eventually reach values up to 10 nm. This shift can be associated with the aggregation of a small number of Ag NPs over time (Fig. 3) [23,24].

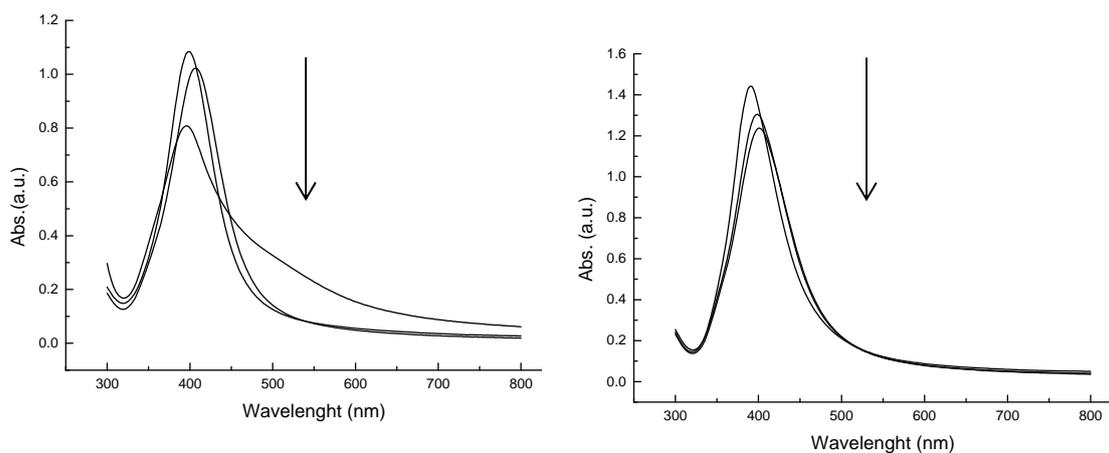


Fig. 3. UV-Vis spectra of Ag NPs obtained using PVP (left) and DME (right), measured over time. The initial measurement is directly after synthesis, and then after 1 and 2 days of storage, plotted from the highest peak intensity to the lowest.

3.2 Effect of an oxidant and reducing agents on prepared Ag NPs

It is well known that most metallic nanoparticles change their reactivity after storage. Their highest reactivity is observed just after synthesis, and active sites that are formed during synthesis become less and less available over time. This process is usually correlated with annealing of the material, but it may also be due to changes that take place at the interface, such as oxidation and reduction processes [25].

In order to induce and study such processes at the interface, we have chosen hydrogen peroxide as an oxidant and hydrazine as a reducing agent. These reagents are simple chemicals that are also used in environmentally friendly redox reactions because they convert into water or nitrogen. The main challenge in a system in which Ag NPs and these reagents are involved, is to find a simple and effective way to visualize the reduction process.

To that end, we use methylene blue dye (Fig. 4), which has a very intense blue color and can be reduced to the corresponding colorless leucoderivative in a reversible reaction. Methylene blue is also commonly used in analytical chemistry as a redox indicator. Any changes in the system will be easy to monitor simply by following the absorbance of the mixture at ~400 nm for Ag NPs and at ~660 nm for methylene blue.

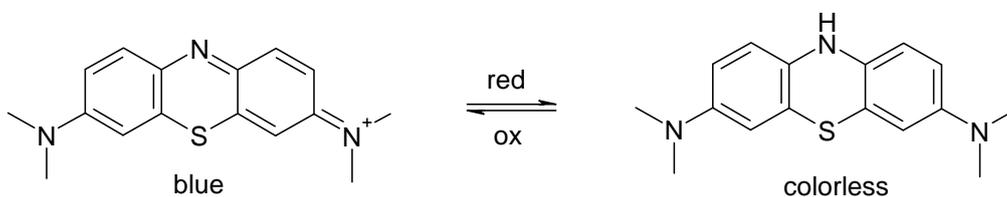


Fig. 4. Reversible redox process of methylene blue.

Literature data show that methylene blue can be easily detected by sensors based on Ag NPs (e.g., a modified evanescent field optical fiber sensor) in a wide range of concentrations. Further, nanocomposites containing Ag NPs are used as a catalyst for photocatalytic degradation under visible light of organic dyes, including methylene blue. In addition,

PVP-protected Ag NPs are successfully used as sensors for hydrogen peroxide and hydrazine [26–28].

First, we studied in separate experiments the effect of the dye and the effect of hydrogen peroxide and hydrazine on Ag NPs. The results show that while both types of Ag NPs seem to be stable against hydrogen peroxide and hydrazine, a decrease in the absorbance of the dye is noticed. Figure 5 shows some representative spectra obtained from PVP- and DME-protected Ag NPs in the presence of methylene blue. The first thing that can be easily observed is the conversion of the dye into its corresponding (colorless) leucoderivative, as evidenced by the peak at $\lambda_{\text{max}} = 662$ nm. The most intense band of the dye at 662 nm is obtained just after mixing, with the intensity decreasing over time. This behavior means that the as-synthesized Ag NPs have a reducing capacity, and are able to convert the methylene blue dye into its colorless form. This reducing capacity is probably due to some borohydride ions that are adsorbed on the NPs surface, which has been mentioned in literature data [22]. It is worth noting that the plasmon band observed in Fig. 5 does not change peak value for PVP-protected Ag NPs, while a small bathochromic shift is clearly visible for DME-protected Ag NPs. For these two stabilizing ligands, PVP is known to afford a better stabilization since it is a polymer that contains nitrogen atoms as well as oxygen atoms. Therefore, it is possible that methylene blue molecules are able to occasionally replace DME ligands on the Ag NPs surface.

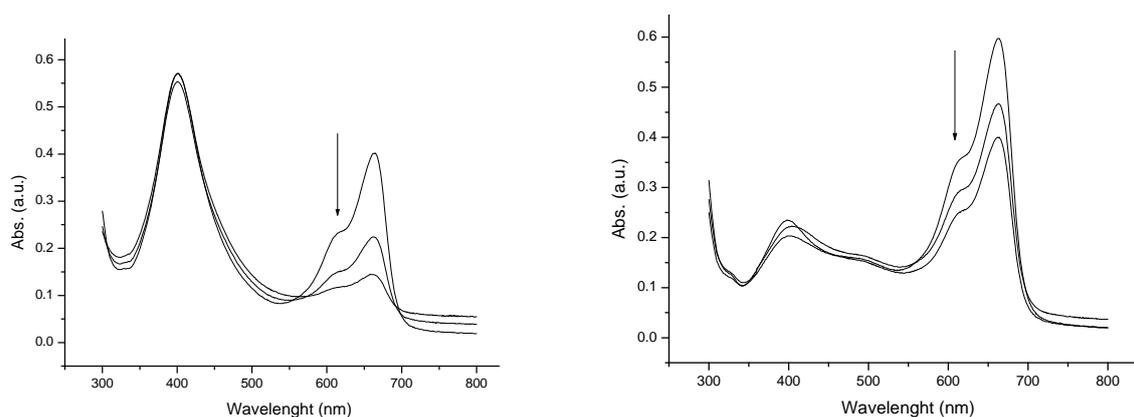


Fig. 5. Typical reduction in the absorbance of methylene blue in the presence of PVP-protected Ag NPs (left) and DME-protected Ag NPs (right) over time. The curves decrease in absorbance with measurements taken initially and after 5 and 10 min.

The next step in our study is to observe the effects of an oxidant on the Ag NPs. Hydrogen peroxide is chosen because of its environmentally friendly, inexpensive and water soluble properties. Interestingly, a marked difference is observed between the two types of Ag NPs (PVP- and DME-protected). Figure 6 shows that for PVP-protected Ag NPs, both bands corresponding to the plasmon resonances of Ag NPs at ~ 400 nm and the dye at ~ 660 nm experience a decrease. For DME-protected Ag NPs, however, the UV–Vis spectra all exhibit an unusual shape, and the intensity of the band corresponding to the dye increases over time.

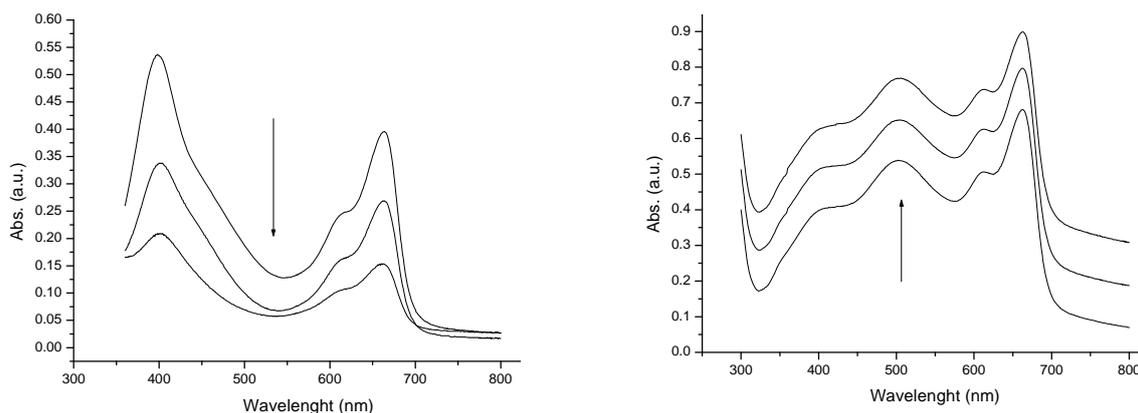


Fig. 6. UV-Vis spectra of PVP-protected Ag NPs (left) and DME-protected Ag NPs (right) in the presence of methylene blue and hydrogen peroxide. The curves decrease (left) or increase (right) in absorbance with measurements taken initially and after 5 and 10 min.

If the process undergone by the PVP-protected Ag NPs strongly indicates reduction of the dye simultaneous with the dissolution of the Ag NPs, probably as silver ions, the DME-protected Ag NPs data indicates that a more complex process is taking place. One of the possible ways to explain the unusual DME-protected Ag NPs absorbance data involves the formation of singlet oxygen. Methylene blue is a known photosensitizer, which activates atmospheric oxygen in the presence of sunlight [29]. In addition, DME is a diether compound, and ethers are generally known for their ease of forming peroxides in the presence of oxygen and light. We stated earlier that Ag NPs are stable against hydrogen peroxide, so the dissolution of these NPs should necessarily involve the presence of the dye. The formation of a new visible band around 500 nm that increases in intensity over time can suggest the presence of a reactive intermediate. At this point, however, no supposition can be made about the nature of this process until further experiments are done.

To obtain more data, the reducing agent hydrazine, chosen because of its environmentally friendly, inexpensive and water soluble properties, was added to the mixture of Ag NPs and dye. The corresponding spectra are shown in Fig. 7.

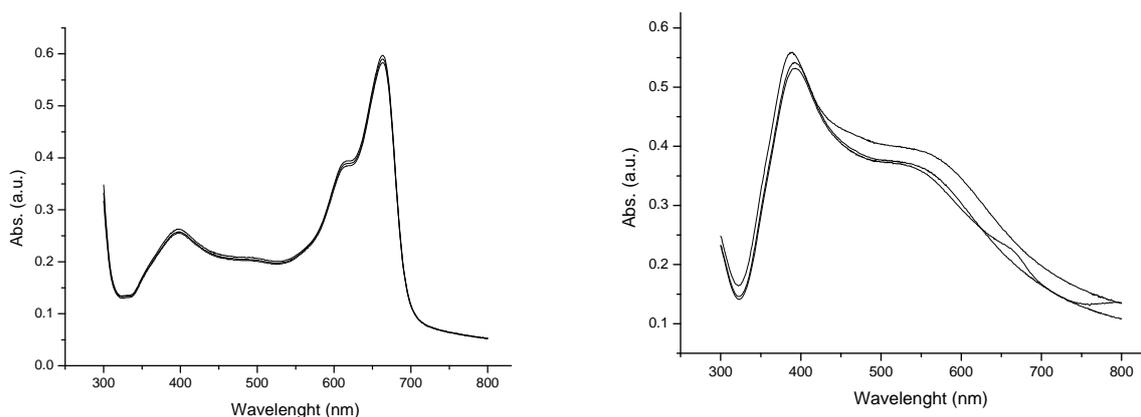


Fig. 7. UV-Vis spectra of PVP-protected Ag NPs (left) and DME-protected Ag NPs (right), in the presence of methylene blue and hydrazine. The curves change very little in absorbance with measurements taken initially and after 5 and 10 min.

It is clearly seen that for both PVP- and DME-protected Ag NPs, very small changes are visible. Hydrazine does not affect the concentration of Ag NPs, as stated previously, nor the methylene blue. The spectra recorded for DME-protected Ag NPs show small differences,

probably related to the higher probability of ligand replacement. As a general remark, therefore, hydrazine is not able to increase the reducing capacity of the Ag NPs.

4. Conclusions

In conclusion, the effect of an oxidant (hydrogen peroxide) and a reducing agent (hydrazine) on the reactivity of PVP- and DME-protected Ag NPs was studied. The results show that both types of Ag NPs have the capacity to reduce methylene blue. Hydrazine and hydrogen peroxide alone are not found to affect the Ag NPs. In the presence of methylene blue, however, hydrogen peroxide leads to the dissolution of the Ag NPs, while hydrazine has little influence.

Acknowledgements

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Supplementary material

Spectra recorded after 1 hour for the PVP- and DME-protected silver nanoparticles in the presence of methylene blue and hydrogen peroxide or hydrazine. IR spectra of the solid nanoparticles are also included.

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Supplementary material

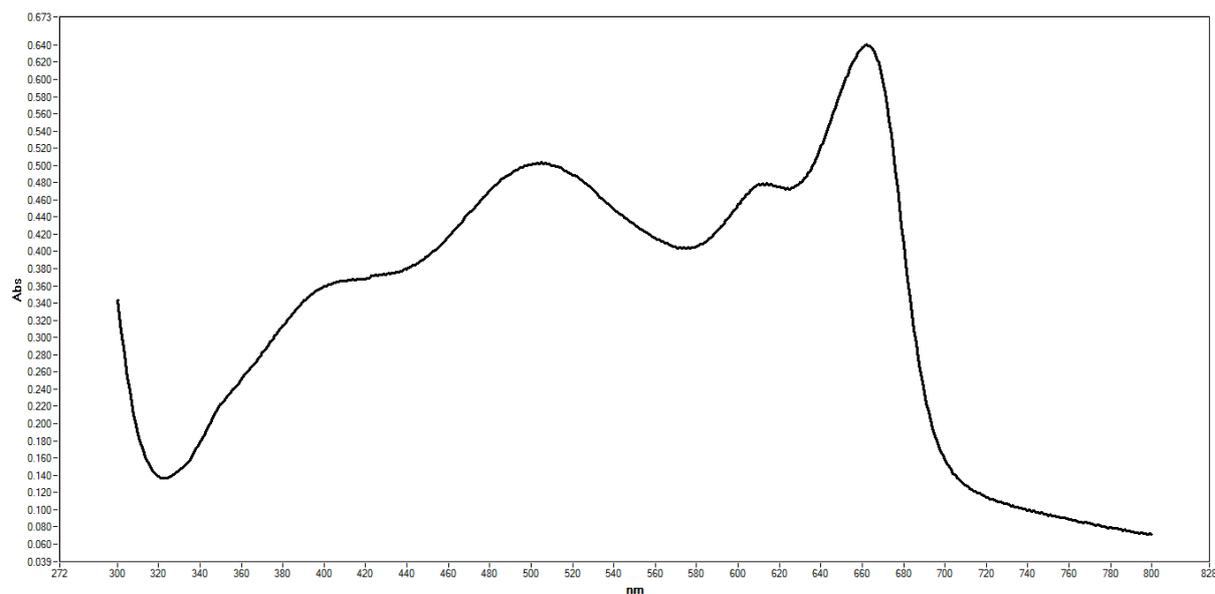


Fig. S1. UV-Vis spectrum of DME protected Ag NPs, in the presence of methylene blue and hydrogen peroxide, recorded after one hour

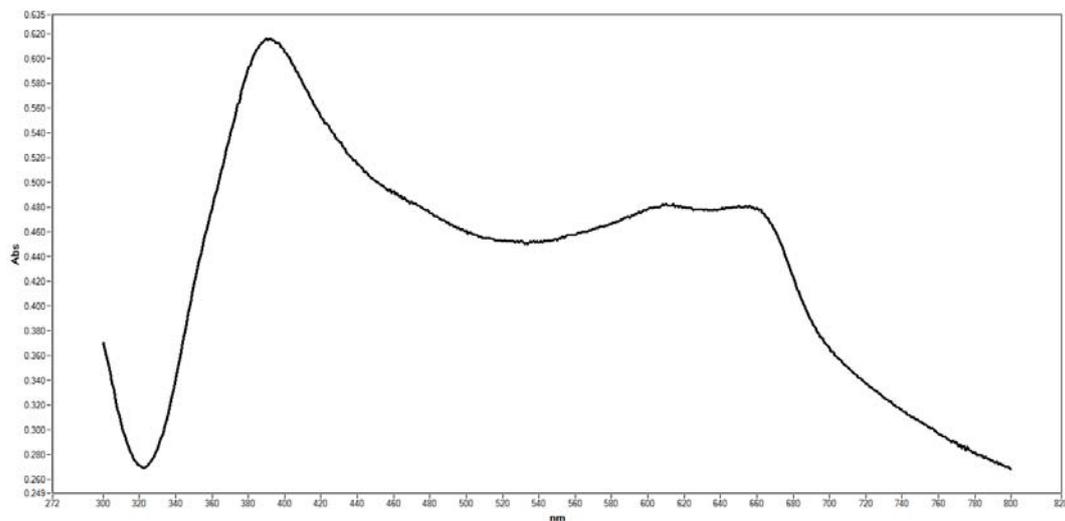


Fig. S2. UV-Vis spectrum of DME protected Ag NPs, in the presence of methylene blue and hydrazine, recorded after one hour

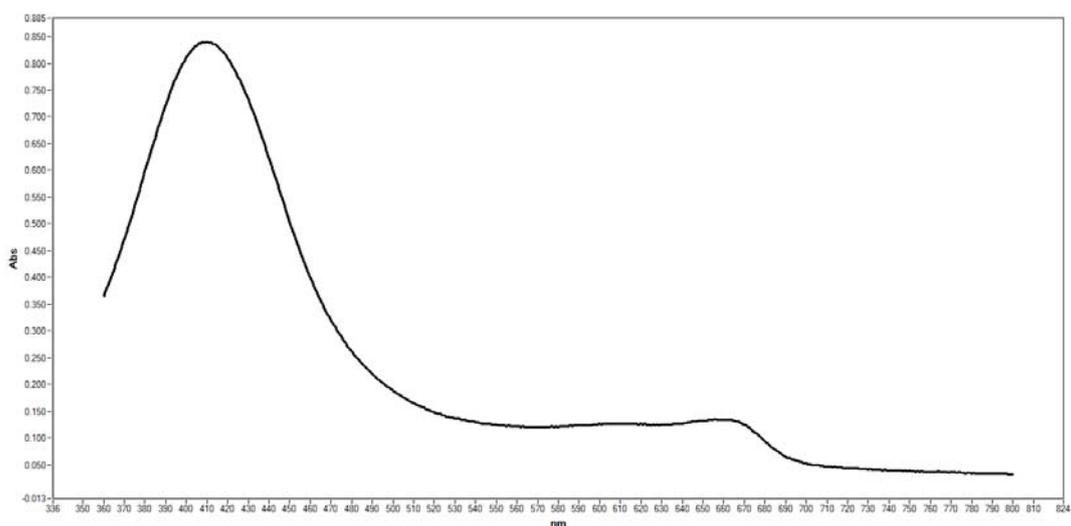


Fig. S3. UV-Vis spectrum of PVP protected Ag NPs, in the presence of methylene blue and hydrogen peroxide, recorded after one hour

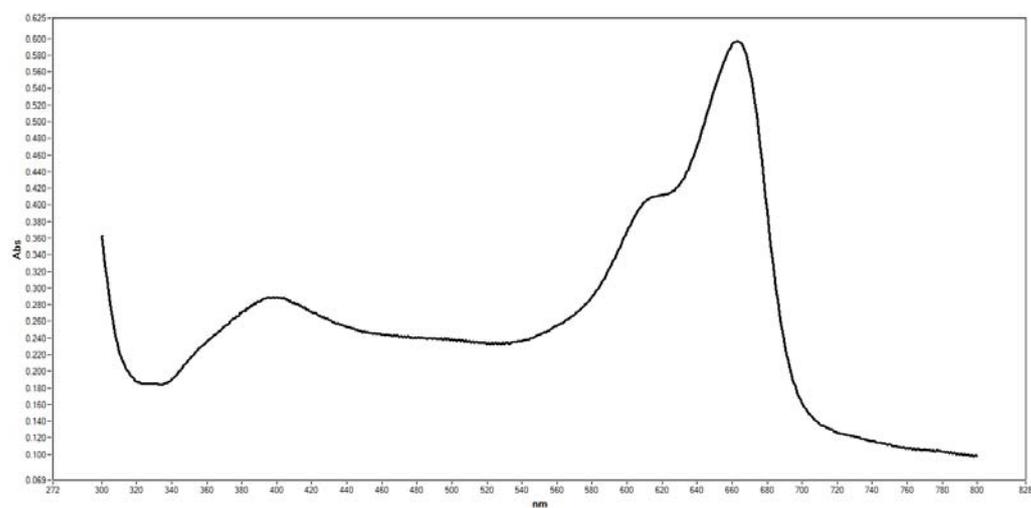


Fig. S4. UV-Vis spectrum of PVP protected Ag NPs, in the presence of methylene blue and hydrazine, recorded after one hour

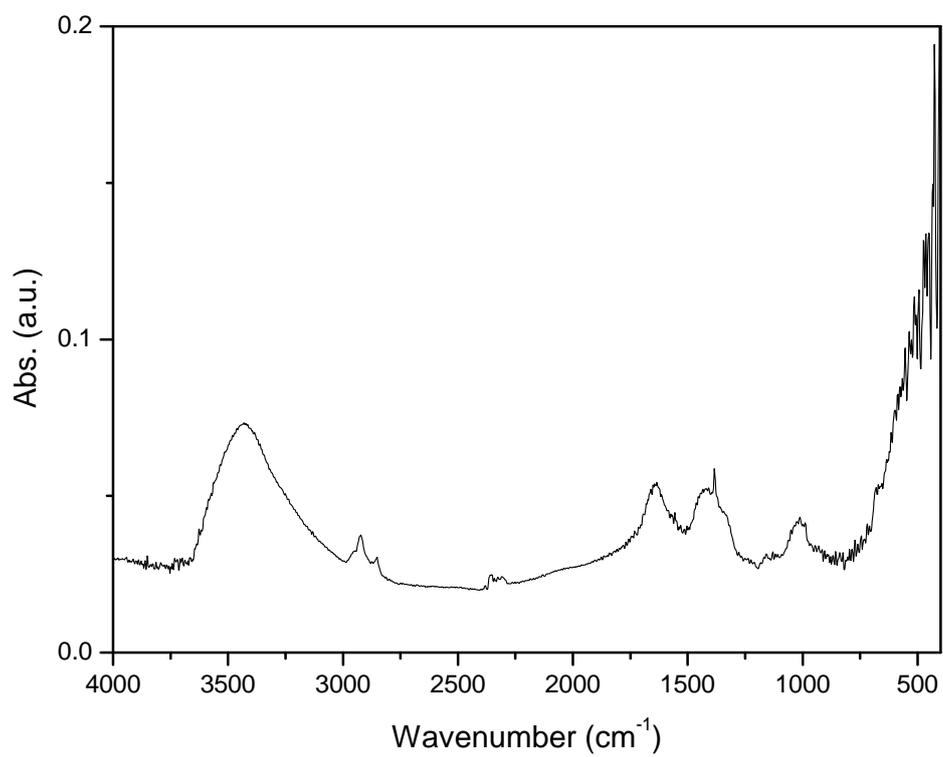


Fig. S5. IR spectrum of Ag NPs obtained using PVP as stabilizer

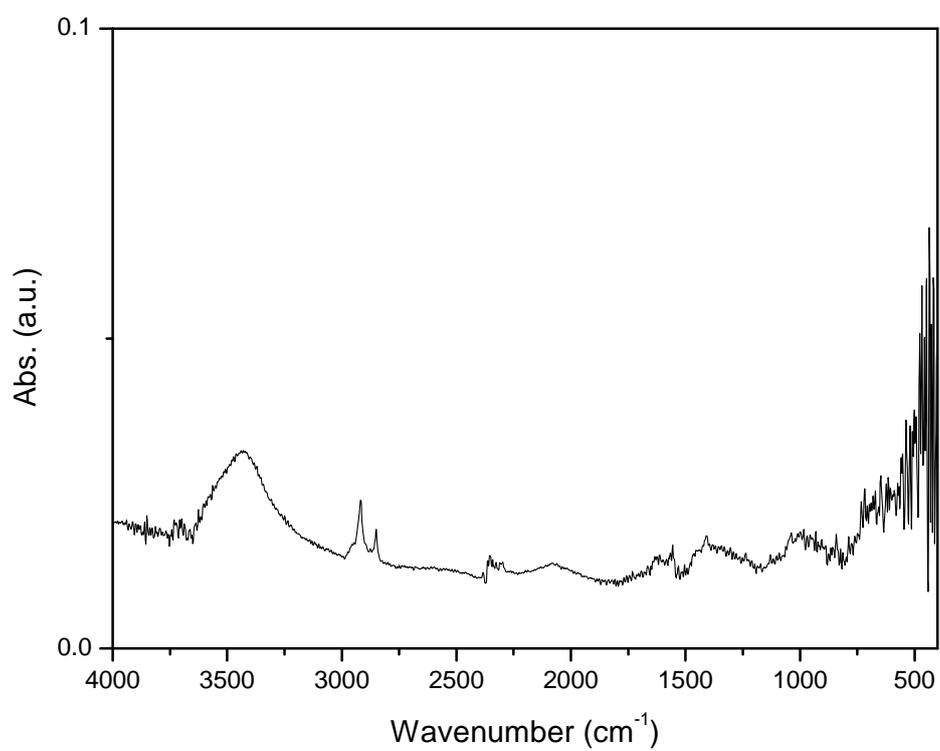


Fig. S6. IR spectrum of Ag NPs obtained using DME as stabilize