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Green preparation and spectroscopic characterization of plasmonic silver nanoparticles using fruits as reducing agents

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Abstract

Chemicals typically available in plants have the capability to reduce silver and gold salts and to create silver and gold nanoparticles. We report the preparation of silver nanoparticles with sizes between 10 and 300 nm from silver nitrate using fruit extract collected from pineapples and oranges as reducing agents. The evolution of a characteristic surface plasmon extinction spectrum in the range of 420 nm to 480 nm indicates the formation of silver nanoparticles after mixing silver nitrate solution and fruit extract. Shifts in plasmon peaks over time indicate the growth of nanoparticles. Electron microscopy shows that the shapes of the nanoparticles are different depending on the fruit used for preparation.

The green preparation process results mainly in individual nanoparticles with a very poor tendency to form aggregates with narrow gaps even when aggregation is forced by the addition of NaCl. This explains only modest enhancement factors for near-infrared-excited surface enhanced Raman scattering.

In addition to the surface plasmon band, UV-visible absorption spectra show features in the UV range which indicates also the presence of small silver clusters, such as Ag_4^{2+} . The increase of the plasmon absorption correlates with the decrease of absorption band in the UV. This confirms the evolution of silver nanoparticles from silver clusters.

The presence of various silver clusters on the surface of the “green” plasmonic silver nanoparticles is also supported by a strong multi-color luminescence signal emitted by the plasmonic particles during 473 nm excitation.

Keywords

fruits, green synthesis, luminescence, plants, plasmonics; SERS; silver cluster, silver nanoparticles

Introduction

Metal nanoparticles in various size ranges play an increasingly important role in many different fields of science, technology and medicine ranging from applications as catalyst, as antibacterial agents in medicine or plasmonic active structures in optical sensing and imaging^{1, 2, 3, 4}. These broad fields of applications generate a strong interest also in the preparation of metal nanoparticles. Many methods have been invented to synthesize nanoparticles, which

can be mainly divided into top down and bottom up processes. Top down processes consist of physical processes where a solid is broken down into nanoparticles as it appears for example during laser ablation of nanoparticles from a macroscopic piece of metal^{5,6}. Nanoparticles made by a physical process such as laser ablation have the advantage of being “chemically clean” with no impurities on their surfaces introduced by the chemical preparation process. In the bottom up approach, nanoparticles are created from even smaller structures such as silver ions, which are the outcome of a chemical process. The most popular process among the bottom up methods might be the preparation of silver and gold nanoparticles in aqueous solution by the reduction of silver and gold salts using sodium citrate or sodium borohydride as reducing agent⁷. Recently it has been identified that also plant extracts have the capability to reduce silver and gold salts and to create silver and gold nanoparticles^{8,9,10,11,10,12}. Many different chemical compounds are present in various parts of different plants. Polysaccharides, phenolics, flavonoids to mention only a few, could serve as reducing and also stabilizing agents (xPark 2011). Overall, using plant materials offers an eco-friendly way to prepare silver- and gold nanoparticles. Moreover, the diversity of chemical composition of plants, i.e. the combination of various reducing and stabilizing agents results in a broad variety of parameters in the chemical preparation process which enables synthesis of many different nanoparticles regarding size and morphology.

Here we study the formation of silver nanoparticles using fruit extract from oranges and pineapples and check their capability as enhancing plasmonic structures for SERS.

We explore the formation of nanoparticles by varying conditions in the preparation process such as ratios of the mixtures of silver nitrate and fruit extracts and the presence or absence of light. Our studies focus on the preparation of nanoparticles between 10 and 100 nm, i.e. a size range which is of particular interest for plasmon-supported spectroscopy, such as surface enhanced Raman scattering.

The formation of silver nanoparticles and their growth is monitored by the increase of the characteristic plasmon absorption of silver around 420-470 nm and shifts of the absorption peak, respectively. Absorption signatures in the UV range which can be assigned to small silver clusters and surface enhanced luminescence spectra collected from the particles can provide information on the evolution process of silver nanoparticles.

Results and Discussion

Silver nanoparticles have been prepared at room temperature by mixing silver nitrate solutions and fruit extracts collected from pineapples and oranges. Evolution of the silver nanoparticles starts a few minutes after adding fruit extract to the AgNO₃ solution and is indicated by the beginning of evolution of a characteristic surface plasmon extinction band. As Figure 1 shows, for orange extract, the peak of the plasmonic band appears at 420 nm with no shift during the growing process. This indicates that the particles are always within the Rayleigh limit ($d \ll \lambda$). The increase of the absorption reflects the increasing number of such small silver particles over time. First indication of a plasmon band appears after about 30 minutes. The formation of particles can continue within time spans up to 1 month and longer. No extinction appears in the red and near infrared¹³ region.

For pineapple extract, the formation of silver nanoparticles is a faster process. The first sign of a plasmonic band can be seen already after 4 minutes and the process stops after 30 minutes. The peak of the plasmon spectrum appears at 450 nm and shows a small red shift over time. This shift indicates that for pineapple extract, not only the number of particles increases over time, but also the size and morphology of the particles change.

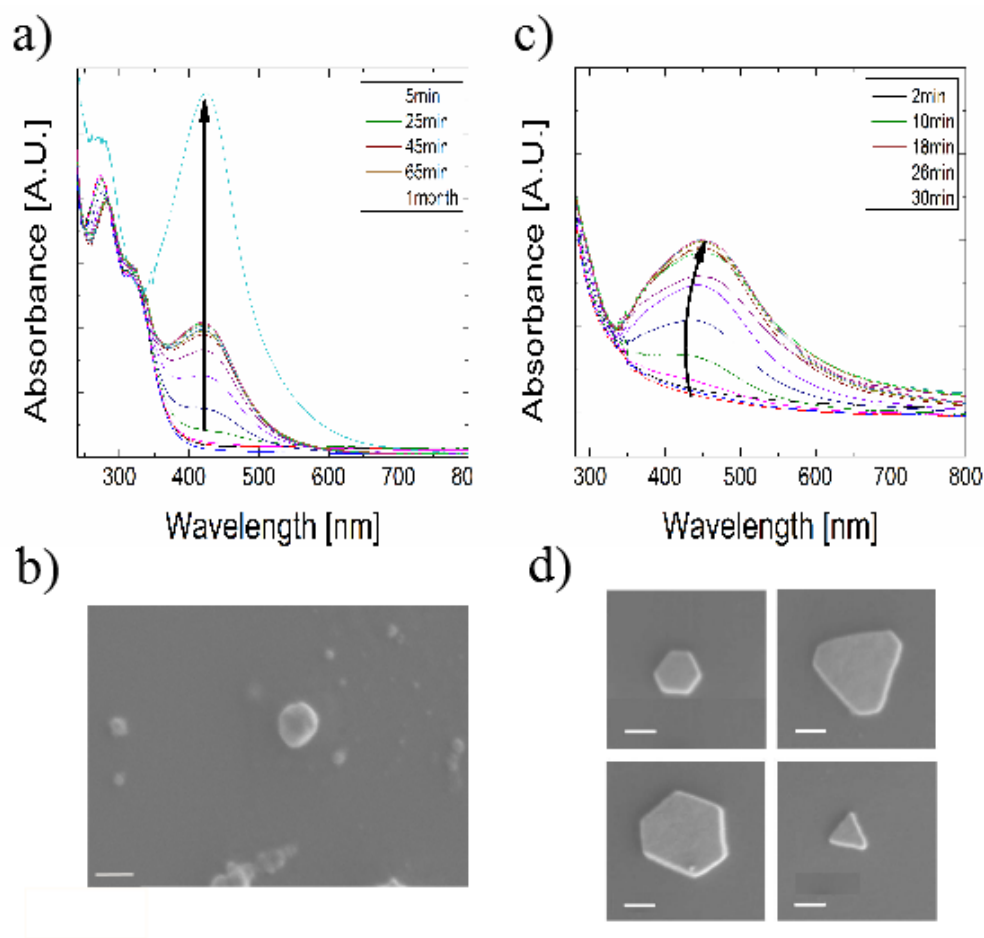


Figure 1: Time evolution of UV-vis spectra of ~1:10 orange extract /AgNO₃ solution between 5 and 75 minutes after mixing and after 1 month (a) and of ~1:50 pineapple extract/AgNO₃ solution between 2 and 30 minutes after mixing (c). The arrows guide the eye between the peaks of the spectra. (b) and (d) show SEM images of typical nanoparticles prepared by using oranges and pineapples, scale bar is 100 nm.

An interesting property of green silver nanoparticles is their capability as enhancing plasmonic structures in SERS, particularly also when excitation in the NIR is used as in many biological applications. High local fields can be generated in small gaps between nanoparticles such as in aggregates¹⁴. The green preparation process used in this study

delivers mainly isolated silver particles and aggregates with relatively wide gaps as it is shown for example in Fig. 2a. for nanoparticles made from orange extract. The extinction spectra in Fig. 2a and the TEM image show that also NaCl at relatively high concentration does not force the formation of aggregates with subnanometer gaps as it had been obtained for other silver nanoparticles. The capability of green silver nanoparticles for enhancing Raman signals in SERS was tested by using NIR excitation and a non-resonant target molecule para mercapto benzoic acid (p MBA). Fig. 2b shows a SERS spectrum of p MBA. The enhancement factor was inferred from a comparison with the normal Raman signal of the molecule. Using excitation in the NIR, the green silver nanoparticles provide only modest enhancement factors between 10 and 100 in agreement with computations of field enhancement factors for individual small silver spheres in the NIR¹⁵. The poor aggregation behavior of the green silver nanoparticles might be explained by the presence of other molecules on the surface of the particles related to plant materials introduced due to the green preparation, which prevent that particles come very close together and even touch each other. Moreover, these residual molecules might prevent that analyte molecules find optimum enhancing places in small distances to the surface of the plasmonic particles.

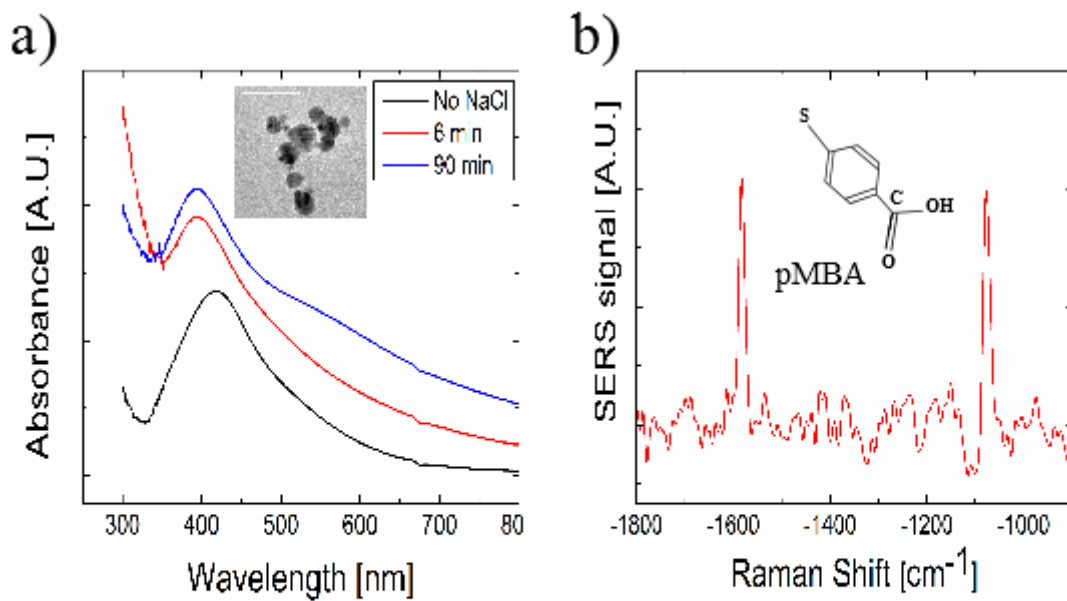


Figure 2: a) Extinction spectra of solutions of green silver nanoparticles before and after the addition of NaCl, final NaCl concentration was 0.2M. The inset shows an aggregate formed by green nanoparticles. b) SERS spectrum of pMBA collected on green silver nanoparticles as enhancing nanostructures using 50 mW excitation at 785 nm.

In general, the main differences in the outcome of the green preparation process are related to the different fruits as it is shown in Fig. 1b and 1d. While orange extract gave rise to round and almost spherical silver particles, reduction by pineapple extract results in particles with sharp corners.

However, not only the kind of fruit determines size, shape and speed of growing of silver nanoparticles, also other experimental parameters during the green preparation process play a role. Figure 3 demonstrates the influence of light on the formation of silver nanoparticles using ananas extract. Fig. 3a shows the evolution of plasmonic particles under exactly the same conditions as used in Fig. 1b. While the process shown in Fig 1b took place in the presence of light, silver particles in Fig. 3a grew in the dark. Fig. 3b shows the increase of the extinction over time in the presence of light and without light in a time scale normalized to the time for achieving the end of the reduction process, i.e. the time when no more increase of the extinction can be observed. The two curves show that the yield of the formation of nanoparticles is higher at the presence of light, but the time behavior in the normalized time scale is very similar. Fig. 3c displays the peak position as a function of normalized time. Also this plot indicates that the chemical process with and without the presence of light might be almost the same. A difference of about 40 nm between the end peak position in both processes indicates that the process without light resulted in larger nanoparticles.

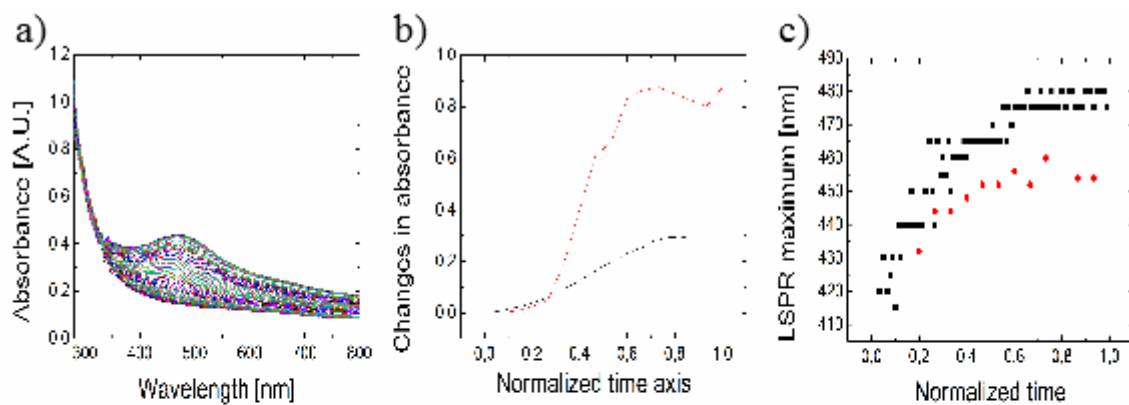


Figure 3: a) Time evolution of UV-vis spectra of ~1:50 pineapple extract/ AgNO_3 solution between 0 and 180 minutes after mixing in darkness, for comparison see Fig 1c that displays the same process in the presence of light . b) Peak growth taken from Figs, 1c and 3a as a function of normalized time. c) Peak position taken from Figs, 1c and 3a as a function of normalized time (red and blue data are with and without light, respectively)

As an additional parameter in the preparation process, we change the volume ratio between the silver nitrate solution and the fruit extract. Figure 4 shows how different ratios of silver nitrate solution and orange extract influence the evolution of silver nanoparticles. The mixture used in Fig. 4b was prepared with an excess of silver nitrate solution over the orange extract compared to Fig. 4a. Fig. 4 shows that the surface plasmon peaks at the same position at 420 nm, i.e. the size and shape of the nanoparticles do not depend on the ratio between silver nitrate and the reducing fruit extract. Much weaker plasmon bands in Fig. 4b indicate that in this experiment, the fruit extract is the limiting factor for the total yield of nanoparticles.

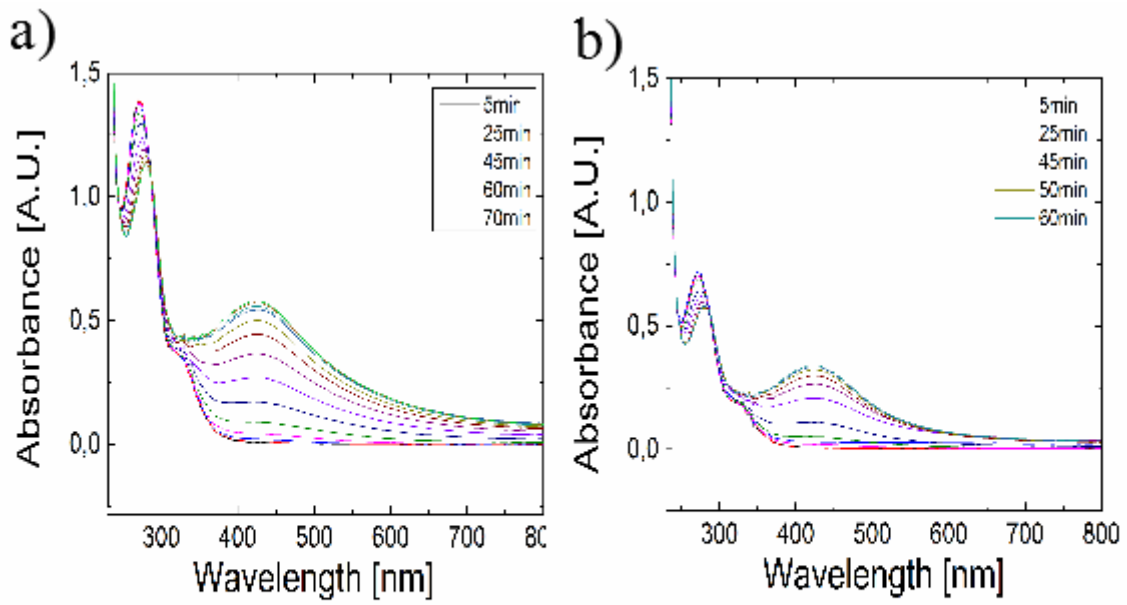


Figure 4: Time evolution of UV-VIS spectra in mixtures of orange extract and AgNO_3 solutions between 5 and 60 minutes after mixing. Figs. 4a and 4b represent different ratios of AgNO_3 solution and orange extract with a 5 times higher ratio of the AgNO_3 solution to plant extract in 4b than in 4a.

In addition to plasmon resonances around 420 nm, the spectra displayed in Figs. 4a, 4b and 1a show peaks in the UV range, which are related to small silver clusters that can be formed from Ag^+ available after the initial reduction process¹⁶. In particular, the observed UV-band at 270 nm can be assigned to Ag_4^{2+} clusters, which, via intermediates Ag_7^{3+} and Ag_8^+ , build up metallic particles Ag_n .¹⁶ Fig. 5 shows that the increase of the plasmon absorption correlates with the decrease of absorption at 270 nm confirming the conversion of silver clusters to plasmonic silver nanoparticles.

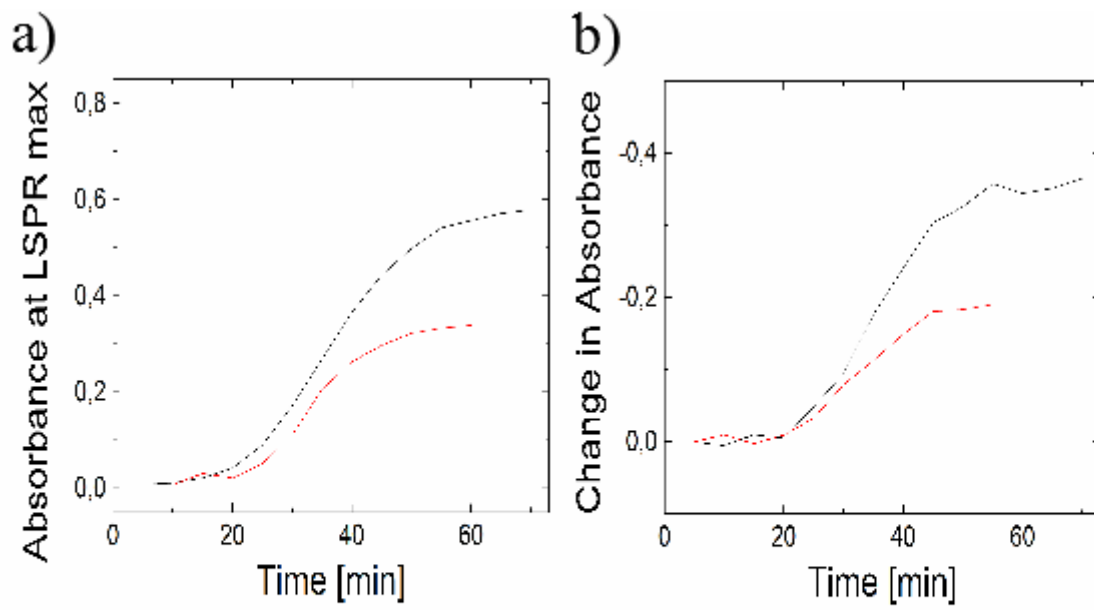


Figure 5: Time evolution of Absorbance at 420 nm and 270 nm related to surface plasmon excitation of silver nanoparticles and Ag_4^{2+} clusters, respectively.

The presence of various silver clusters on the surface of the “green” plasmonic silver nanoparticles is also supported by a strong multi-color luminescence signal emitted by the plasmonic particles during visible excitation. Strong luminescence signal from silver clusters have been reported for the first time in ref. ^{17, 18}. Here we excite plasmonic silver particles using 473 nm light, provided by a 20 mW laser diode through a 100x oil immersion objective. The Emission appears over a wide wavelength range with a strong contribution in the yellow-green region. At some places, the luminescent light shows strong fluctuations (see movie in supporting info xx). This blinking hints to surface-enhanced emission of individual single emitters on the surface of plasmonic silver nanoparticles.

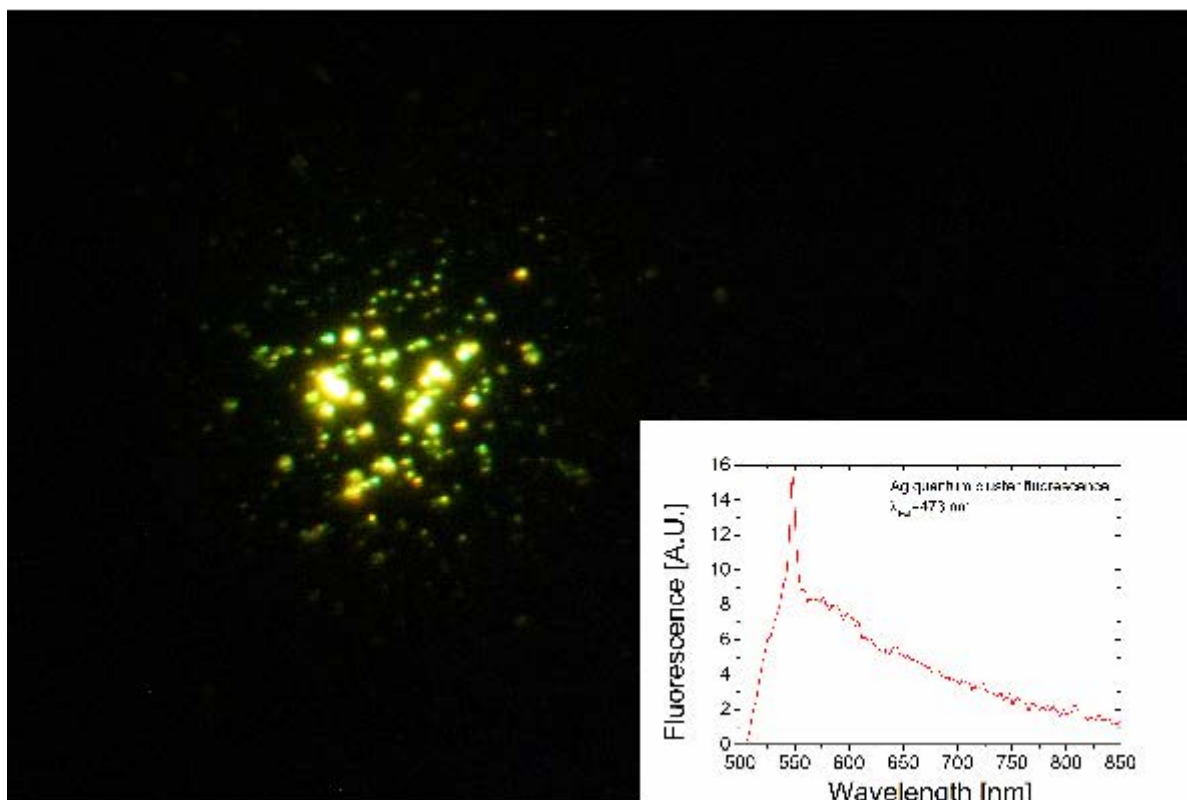


Figure 6: Image and spectrum of multi-color luminescence collected from green silver nanoparticles during 473 nm excitation. The illuminated spot is around $10 \mu\text{m}^2$.

Conclusion

Silver nanoparticles can be prepared in a relatively simple way by using extracts of oranges and pineapples as reducing agents. Size and shape of the particles depend mainly on the kind of fruit used in the chemical preparation process. The UV-VIS absorption spectrum displays the surface plasmon resonance and also features in the UV, which can be assigned to small silver clusters. The correlation between the evolution of the surface plasmon band and the decrease of the silver cluster band in the UV confirms the conversion of silver clusters to plasmonic silver nanoparticles. Remaining single small silver clusters on the surface of the plasmonic nanoparticles give rise to a strong surface enhanced multi-color luminescence.

Experimental

Preparation of fruit extract

Ananas comosus: The pineapple extract was prepared by cutting away all parts except the yellow pulp of the pineapple. This was then sliced and blended after which the pulp was filtered through a standard coffee filter twice resulting in a yellow juice.

Citrus sinensis: The orange extract used in Fig.1 was prepared by taking an orange peel and washing it with demineralized water. Then it was incised into small pieces. 4g of these pieces were added to 40mL of demineralized water. This solution was then heated and stirred in a boiling water bath for 3min. After this, it was cooled under stirring for 3 min and then filtered through a standard coffee filter followed by a 2 μm filter. The orange extract used in Fig.4 was made in exactly the same way with the difference that the 4g of material were taken from only the white part of the orange peel.

All fruits were bought from the local supermarket. The pineapple came from South America. The oranges, sort "Valencia", came from Italy, where they were grown without the use of pesticides.

Acknowledgement

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