HIGHLY SERS ACTIVE GOLD NANOPARTICLE ASSEMBLIES OF CONTROLLABLE SIZE OBTAINED BY HYDROXYLAMINE REDUCTION AT ROOM TEMPERATURE

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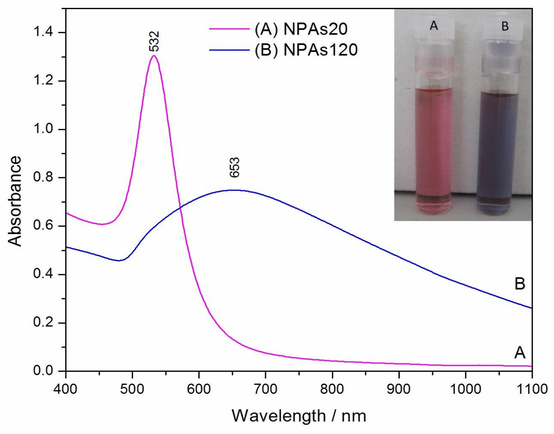
Introduction

In recent years metal nanoparticle synthesis has evolved substantially, now being possible to control their shape, size and surface chemistry. Gold nanoparticles are one of the most important types of nanoparticles with biomedical application, due to their utilization in live tissue as contrast agents, delivery vehicles, therapeutics etc [1]. Nanoparticles are known to self-assemble into larger structures during the growth processes, which are governed by a delicate balance between electrostatic repulsion and Van der Waals attraction [2]. Many nanoparticle superstructures with new properties and applications have been developed, mimicking the behavior of efficient natural machines (e.g., enzymes, proteins, biopolymers, or viruses) [3].

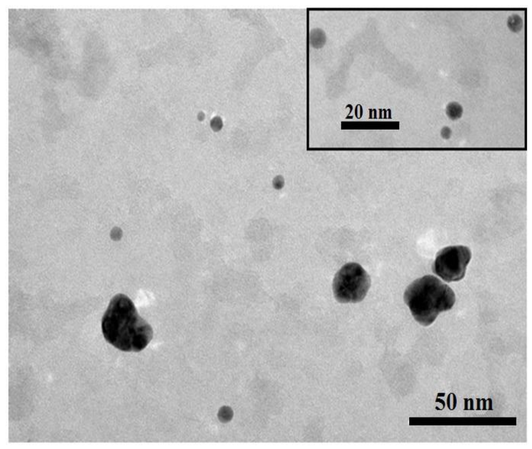
Methods

A novel synthesis approach for gold nanoparticles assemblies (NPAs) at room temperature is proposed in this study. The nanoparticles were prepared at room temperature using hydroxylamine as reducing agent. By varying the experimental conditions, two main nanoparticles categories can be obtained, NPAs20 and NPAs120. Moreover, by stabilizing the colloid with bovine serum albumin (BSA) at different time moments after synthesis, NPAs of controlled size between 20 and 120 nm, could be obtained. The characterization of the nanoparticles were carried out by using UV-Vis, TEM and surface-enhanced Raman scattering (SERS) spectroscopy. The above proposed nanoparticles were internalized into A549 cells by cellular uptake then Raman spectra were collected from fixed cells. The data was processed using PCA in order to create cellular Raman maps for nanoparticle localization.

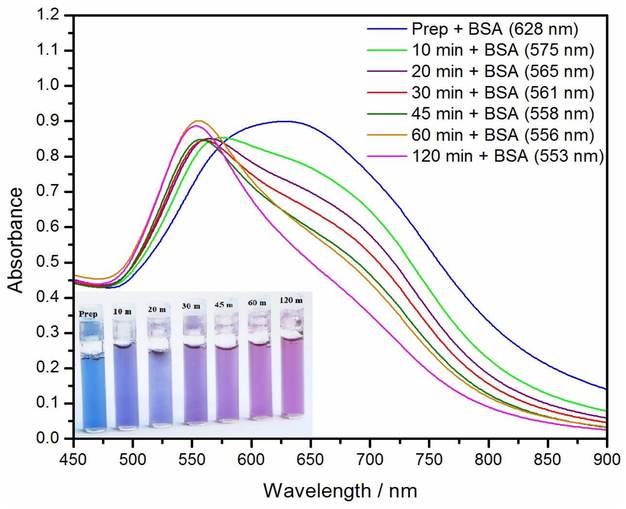
Results A: Nanoparticle characterization



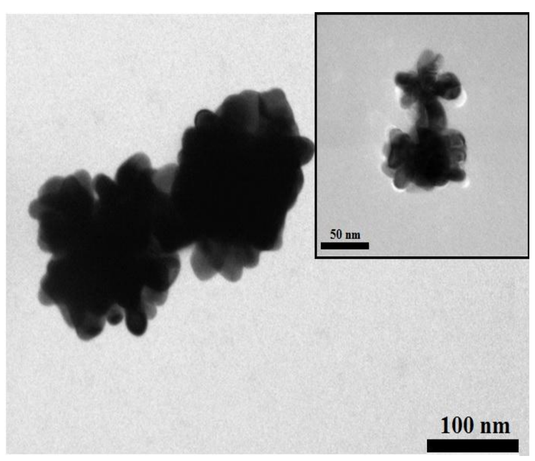
UV-Vis spectra of NPAs20 (A) and NPAs120 colloids (B) recorded one day after preparation.
The inset image shows a picture of the two colloids.



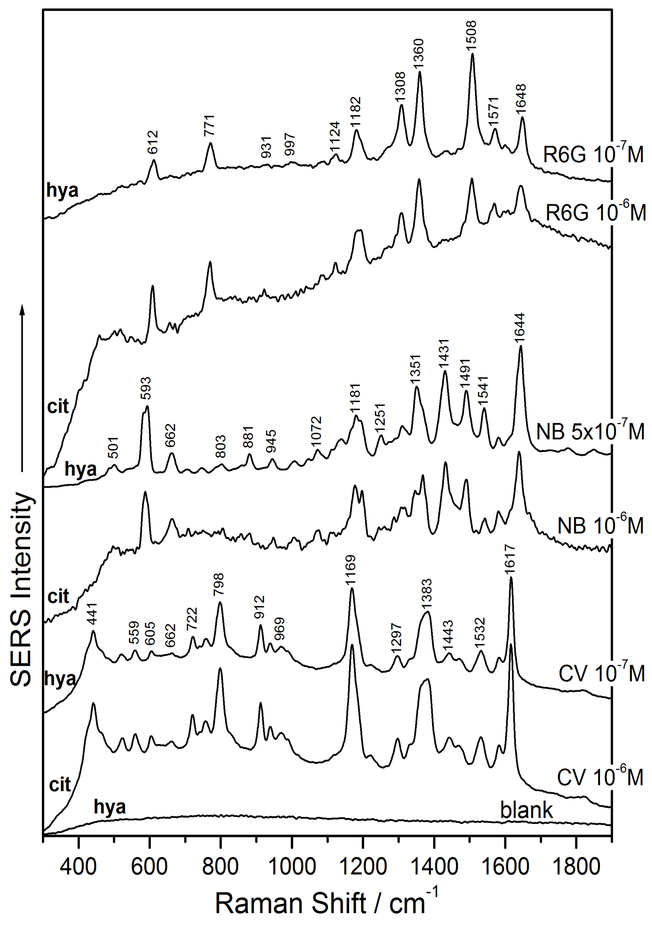
TEM images of the NPAs20 colloid



UV-Vis absorption spectra of the NPAs20 colloid, recorded one week after stabilization with albumin. The inset image shows a picture of the albumin stabilized gold colloids.

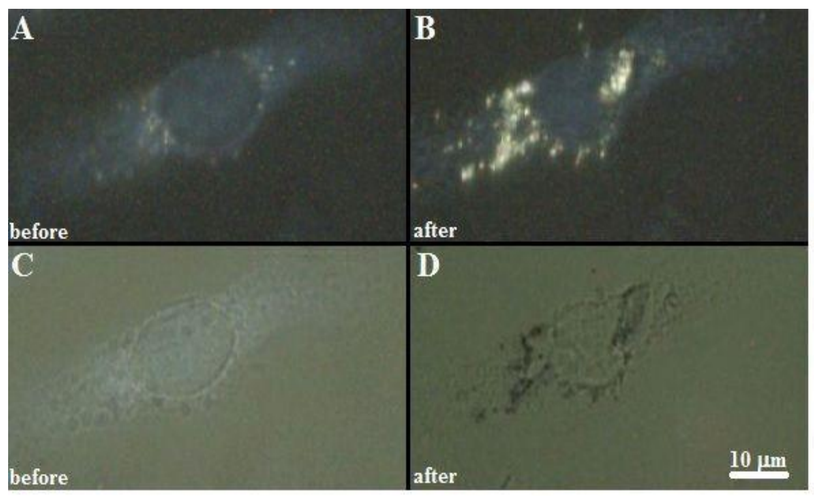


TEM images of the NPAs120 colloid

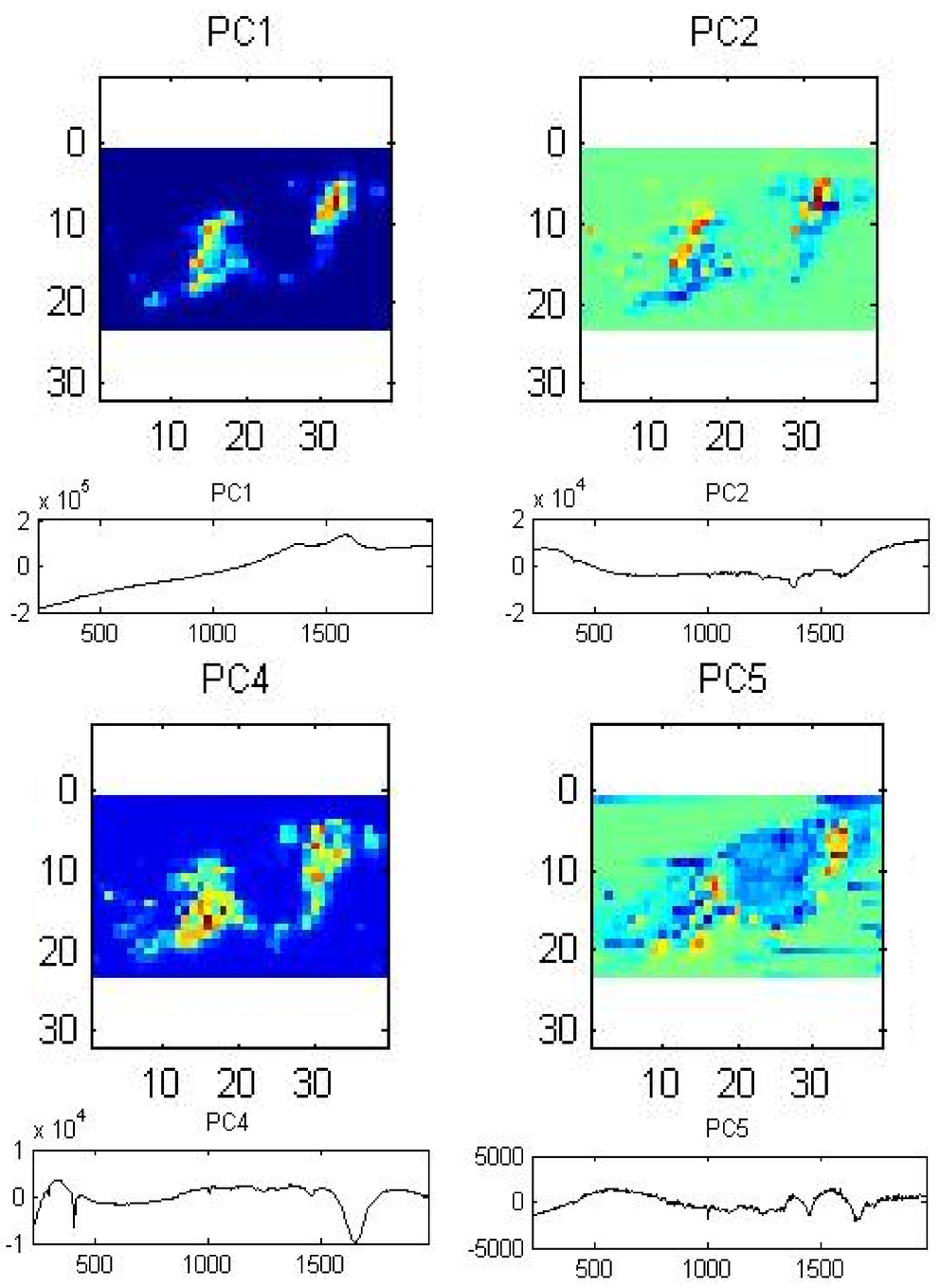


SERS spectra of Crystal Violet (CV), Niel Blue (NB) and Rhodamine 6G (R6G) obtained by using hydroxylamine (hya) and citrate (cit) reduced gold colloids. The analyte concentrations are indicated for each spectrum in the figure.

Results B: Raman map



Light microscopy images in dark field (A,B) and bright field (C,D) illumination before and after laser irradiation



Raman maps of the most relevant principal components after PCA analysis, and their respective spectrum

Conclusion

A new, effective and simple procedure for preparing gold nanoassemblies with mean diameters of 20 and 120 nm based on reduction with hydroxylamine hydrochloride has been described. By surface modification with bovine serum albumin at different time moments after synthesis, highly stable nanoparticle assemblies of controllable dimension can be obtained. SERS spectra at 10^{-7} M analyte concentration were recorded using the 20 nm hydroxylamine reduced nanoassemblies as substrate, showing a better SERS enhancement property, compared to conventional citrate reduced colloidal nanoparticles. Due to the irregular, popcorn like shape the 120 nm nanoassemblies show absorption in the NIR spectral region, a feature which provides them potential for photo-thermal application. Raman spectroscopy appeared to be a useful tool for nanoparticle localization, moreover the laser energy was absorbed and transformed into heat by nanoparticles which led to localized cell damaging.

Acknowledgements

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References

1] E. C. Dreaden, et al., Chemical Society Reviews 41, 2740-2779 (2012).
[2] Y. Xia, et al., Nature Nanotechnology 6, 580-587 (2011).
[3] B. Pelaz et al., ACS Nano 6, 8468-8483 (2012).