
Nanofabrication, Characterization and Modelling of Au Nanoparticles

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Abstract: The aim of this work is the characterization and modelling of spherical gold nanoparticles synthesized in laboratory by Turkevich method. In the first place, an absorbance optical measurement was performed on the colloidal solution. The experimental data were modelled using the extinction cross section from the Mie theory, in order to obtain an estimate of the radius of the particles, its density and the refractive index of the medium. A Grazing-incidence X-ray Diffraction was performed on the nanoparticles deposited on a Si substrate, to get information about the nanoparticle size and its structure. At last a Scanning Electron Microscope was used to directly measure particle radius and get information about their size distribution.

Key words: *Au Nanoparticles, Mie Theory, Optical Characterization, X-Ray Diffraction, SEM Analysis.*

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1 Introduction

Nanoparticle research has greatly expanded over the past decades. In particular, a major effort was put in the study and control of the shape and of the size of nanoparticles because of their influence over the electro-magnetic and optical properties of the nanoparticles.

Gold nanoparticles are nanoparticles of special interest due to their prominent optical resonance in the visible range.

The Au nanoparticles' interaction with light is strongly dictated by their environment, size and physical dimensions. Oscillating electric fields of a light ray propagating near a colloidal nanoparticle interact with the free electrons causing an oscillation of electron charge that is in resonance with the frequency of visible light. These resonant oscillations are known as surface plasmons.

The aim of this work is to describe and characterize colloidal spherical gold nanoparticles.

In the first part of this paper we will illustrate the main steps of the synthesis of the Au nanoparticles by means of the *Turkevich method* (**Section 2**).

After the synthesis we obtained the optical spectrum of the gold nanoparticles in the Vis-NIR range using a JASCO V670 spectrophotometer in order to simulate the absorption line and the Mie extinction cross-section by means of the Mie theory in the dipolar approximation and of the size-corrected experimental dielectric function of Au (**Section 3**).

The optical analysis of the gold nanoparticles allowed us to obtain informations on the size of the nanoparticles, on their concentration and on the refractive index of the medium.

We performed then independent measurements on the average size of spherical gold nanoparticles using the Grazing incidence X-Ray Diffraction (XRD): we estimated the diffraction of X-rays photons, coming from $\text{Cu}_{K\alpha}$, forming an angle of 2θ with respect to the incoming beam (**Section 4**).

In the end, in **Section 5**, we used a scanning electron microscope (SEM) to perform a statistical size distribution of the system.

2 Synthesis of Au nanoparticles

Colloidal spherical gold nanoparticles can be synthesized via the Turkevich method: gold atoms are decomposed from a gold acid precursor forming a supersaturated solution and thus initiating the nucleation of the nanoparticles aggregating and growing under controlled constant temperature.

This method is able to archive particles sizes of $10 \div 20$ nm of diameters.

2.1 Turkevich method

The main steps which determine the Turkevich method can be summed up as follows:

1. Pour in a beaker 9.5 mL of gold hydrochlorate solution (HAuCl_4);
2. Cover the beaker with the watch glass;
3. Suspend the beaker in the crystallizer filled with normal water on the hot plate and rise the temperature up to 100°C ;
4. Activate the stirrer in order to obtain an homogeneous distribution of temperature and concentration;
5. Heat the sodium citrate solution ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) up to 100°C ;
6. When both solutions are at 100°C , add 0.5 mL of the $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ solution to the beaker, which will decomposes the precursor by redox reduction in order to reduce gold atoms to metallic gold. The citrate concentration is chosen to prevent the formation of big structures;
7. Wait 15 minutes with the stirrer on and at 100°C .

The result we obtained can be seen in **Figure 1**.



Figure 1: Sample of colloidal Au nanoparticles we obtained in the laboratory using the Turkevich method.

3 Optical Characterization

In order to acquire the optical spectrum of the colloidal Au nanoparticles we used a JASCO double beam spectrophotometer, which shines light in a continuous spectrum in the Vis-NIR range ($300 \div 2700$ nm).

To verify the presence of the localized surface plasmon resonance (LSPR) we acquired the absorbance spectrum: the spectrophotometer shoots on the sample a single wavelength at a time which is selected by a monochromator and then the same procedure is repeated for a second beam, which provides a base-line. At this point the transmittance T is measured and then converted, using the Lambert-Beer equation (Equation 1), into absorbance data (A):

$$A := \log_{10} \frac{1}{T} = \log_{10}(e) z \sigma_{ext} \rho \quad (1)$$

where $z = 1$ cm is the length of the sample, σ_{ext} is the Mie extinction cross section and ρ is the density of the nanoparticles.

The experimental data we obtained are plotted in **Figure 2**. As can be seen, the spectrum exhibits a resonant behavior, and data near the peak can be used to estimate various properties of the system.

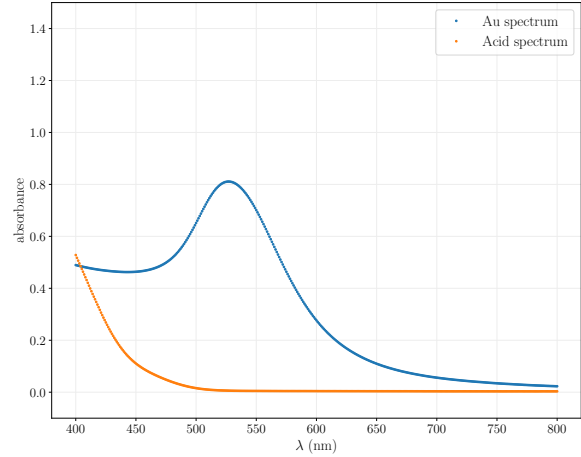


Figure 2: Experimental spectra: in blue is plotted the Gold nanoparticle experimental spectrum, while in orange the acid spectrum.

The label *Acid spectrum* of **Figure 2** refers to the fact that in the first place we measured the optical spectrum of the medium in which nanoparticles were immersed, (which was water and tetrachloroauric acid), and then we acquired the gold nanoparticle solution spectrum (*Au spectrum* label).

The following optical analysis has been performed in the $400 \div 800$ nm range.

3.1 Model

We can model this spectrum using the extinction cross section coming from Mie Theory in dipolar approximation, upon some assumptions:

- we assume that the system is monodispersed with respect to the particle radius;
- the nanoparticle dimension is much smaller than the injected wavelengths: $R \ll \lambda$;
- we assume a regime of independent nanoparticles: particles are not affected by each other scattering field;
- the medium dielectric function is real: $\epsilon_m(\omega) \in$

\mathbb{R} ;

- the nanoparticle dielectric function is size-dependent according to the following equation:

where ω_P is the plasmon frequency of bulk gold, $\Gamma(R) = \Gamma_\infty + \pi v_{Fermi}/4R$ is the size-dependent electrons relaxation frequency according to Drude model and Γ_∞ is the relaxation frequency in bulk gold.

$$\epsilon(\omega, R) = \epsilon(\omega, \infty) + \omega_P^2 \left(\frac{1}{\omega^2 + \Gamma_{bulk}^2} - \frac{1}{\omega^2 + \Gamma(R)^2} \right) - i \frac{\omega_P^2}{\omega} \left(\frac{\Gamma_{bulk}}{\omega^2 + \Gamma_{bulk}^2} - \frac{\Gamma(R)}{\omega^2 + \Gamma(R)^2} \right) \quad (2)$$

electron concentration of gold from [2]

Table 1: Bulk constants of gold at room temperature [2], v_{fermi} da [1].

ω_P [Hz]	Γ_{bulk} [Hz]	v_{Fermi} [m/s]
$1.38 \cdot 10^{16}$	$1.08 \cdot 10^{14}$	$1.40 \cdot 10^6$

Size correction for ϵ . From the Drude model for the electrons of the metal one can derive the following:

$$\epsilon_1(\omega, R) = \epsilon_1(\infty) + \omega_P^2 \left(\frac{1}{\omega^2 + \Gamma_{bulk}^2} - \frac{1}{\omega^2 + \Gamma(R)^2} \right)$$

$$\epsilon_2(\omega, R) = \epsilon_2(\infty) - \frac{\omega_P^2}{\omega} \left(\frac{\Gamma_{bulk}}{\omega^2 + \Gamma_{bulk}^2} - \frac{\Gamma(R)}{\omega^2 + \Gamma(R)^2} \right)$$

where $\omega = c/\lambda$, R is the radius of the nanoparticle, ω_P is the bulk plasmon frequency and Γ is the typical damping time for electrons. With semiclassical computations one can find that

$$\Gamma(R) = \Gamma_{bulk} + q \frac{v_F}{R}$$

where v_F is the Fermi velocity for electrons and $q = \pi/4$ in the assumption of spherical nanoparticles. The size correction of the dielectric function is illustrated in **Figure 3** for different values of the radius.

$$A = C \rho \epsilon_m^{3/2} R^3 \frac{\epsilon_2}{(\epsilon_1 + 2\epsilon_m)^2 + \epsilon_2^2} \quad (3)$$

with $C = \log_{10}(e) \frac{9}{c} \frac{4\pi}{3}$

scrivi che abbiamo diviso in due parti, una variando R e ρ e con ϵ_m costante e poi per la coppia R e ϵ_m

We notice that a model with a size-independent value for gold dielectric constant $\epsilon(\omega)$ is useless, because the equation 1 contains the product of R and ρ , so the parameters cannot be computed independently. Hence, we directly use a size-dependent equation, considering $\epsilon_1(\omega, R)$ and $\epsilon_2(\omega, R)$.

In order to simulate the experimental absorbance, we vary the values of the three parameters R , ρ and ϵ_m inside suitable ranges as follow:

$$\chi^2 = \left(\frac{A_{exp} - A_{sim}}{\sigma_{A_{exp}}} \right)^2 \quad (4)$$

with $\sigma_{A_{exp}} = 1/A_{exp}$

Where $\epsilon_m = 1.33^2$ which is the refractive inde of water to the square

In order to simulate the experimental absorbance, we vary the values of the three parameters R , ρ and ϵ_m inside suitable ranges as follow:

- at first, we vary R and ρ keeping ϵ_m constant. Thus, we obtain the fit for the couple (R, ρ) ;
- then, we find the values minimizing the χ^2 function, which is defined as follow:

$$\chi^2 = \left(\frac{A_{exp} - A_{sim}}{\sigma_{A_{exp}}} \right)^2 \quad (5)$$

where $\sigma_{A_{exp}} = 1/A_{exp}$ is the error associated to the experimental absorbance. We choose this value for the error in order to give a different weight to the spectrum values and eventually obtain a better agreement between data and simulation;

- we fix the value of ρ^* obtained from previous simulation and vary R and ϵ_m , obtaining the fit for the couple (R, ϵ_m) . Again, we compute the minimum χ^2 for these parameters;
- the value of ρ^* from the first minimization and the values of R^* and ϵ_m^* from the second minimization are the final parameters;

We compute the filling fraction $f = \rho V$ in order to verify the assumption of non-independent particles.

3.2 Results

At first, we simulate the spectrum for the couple (R, ρ) , fixing as dielectric constant for the medium the water one, $\epsilon_m = 1.33^2$. As we expect an average radius between 5 and 10 nm, we vary R inside the range $[3 : 15]$ nm, whereas for ρ , we make a preliminar trial in order to find its magnitude order. A suitable range obtained is $[1, 10] \cdot 10^{-9} \text{nm}^{-3}$. The simulated spectrum obtained from this first fit has not a good agreement with the experimental one, as illustrated in Fig.??.

Then, we make the fit for (R, ϵ_m) couple. We vary R in the same range as before, while for ϵ_m we choose $[1.5 : 2.5]$. From this second fit, we get a value for ϵ_m^* quite different than the one we fixed in the (R, ρ) fit. This improves the agreement with the experimental spectrum (Fig.??), even if there is still a poor fit quality for low λ . This may be due to the non-absorbing medium approximation: as shown in Fig.??, the absorbance for low wavelengths is quite high.

The obtained values are:

$$R^* = \text{nm}, \quad \rho^* = \cdot 10^{-9} \text{nm}^3, \quad \epsilon_m^* =$$

In order to verify the stability of our parameters, we plot the χ^2 map as a function of the two couples

of parameters (R, ρ) and (R, ϵ_m) . The two maps are illustrated on the bottom of Fig.??.

From the (R, ρ) plot, we observe that we do not get an isolated minimum for χ^2 , but there is an elongated region with low χ^2 . This may be due to the correlation between R and ρ in the absorbance formula. In the (R, ϵ_m) plot of χ^2 , we can see that the stability region is more sharp, so the value for ϵ_m is probably more precise. We try to associate to these estimates an error coherent with these χ^2 maps, but, especially for the density, the uncertainty is very high; giving an estimate with such a big error is probably meaningless.

To summarize, from this analysis, the best values for the three parameters R, ρ, ϵ_m are:

$$R^* = \text{nm}, \quad \rho^* = \cdot 10^{-9} \text{nm}^3, \quad \epsilon_m^* =$$

Since the filling fraction results $f = 2.4 \times 10^{-6}$, the assumption of independent particles holds. Indeed, the distance between particles is so high that single scattering events can be considered. We can also justify the dipolar approximation, since the particle radius is less then 20 times smaller than the wavelength.

Moreover, the best value for the position of the peak is $\lambda^* = 529 \text{nm}$ which agrees with the Mie theory.

Eventually, we repeat the analysis by assuming a log-normal size distribution. In Fig.?? we report the histogram for the log-normal centered in the average radius $R^* = 5.455$, found by the previous analysis, and with $\sigma = 0.1$. However, the agreement of the simulated spectrum obtained with the size-distribution does not improve with respect the one of a monodispersed system.

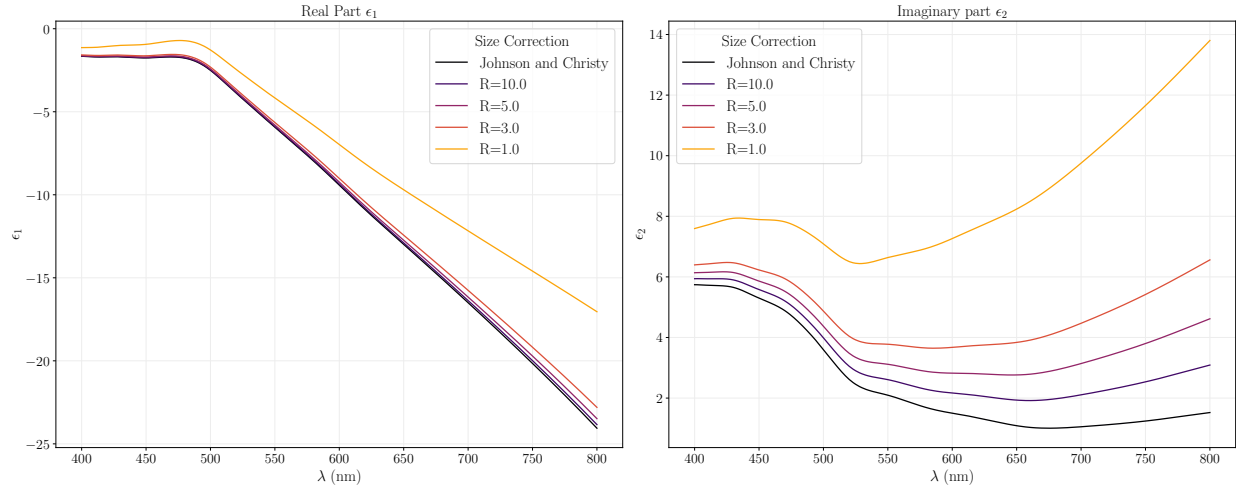


Figure 3: Size correction of the dielectric function for different values of the radius. Johnson and Christy label refers to non size corrected dielectric values. *umenta caratteri immagine - ok?*

qui scrivo

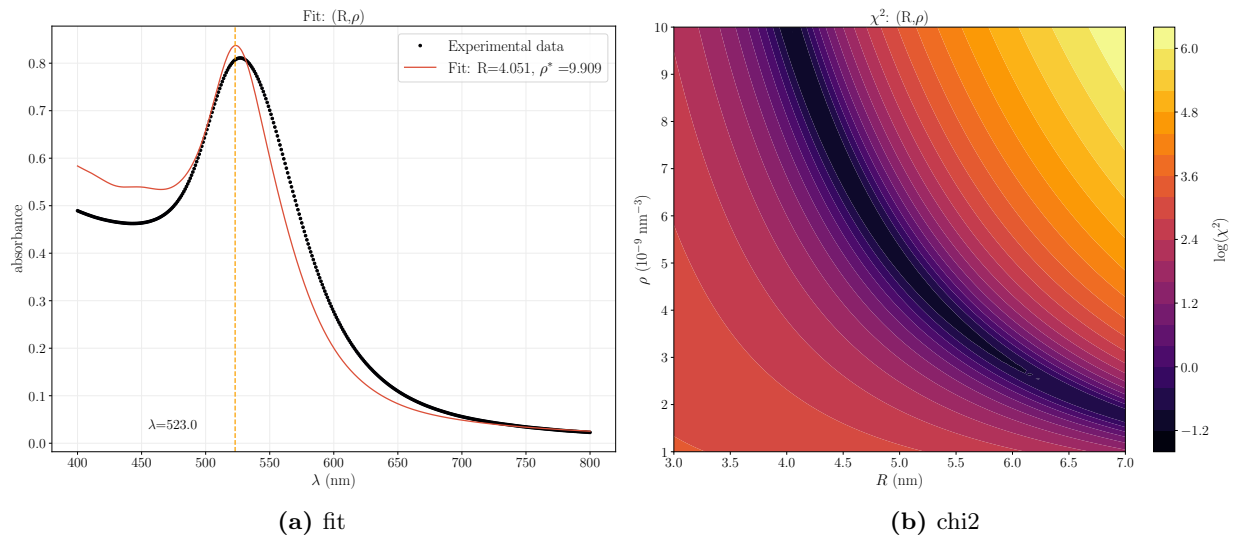
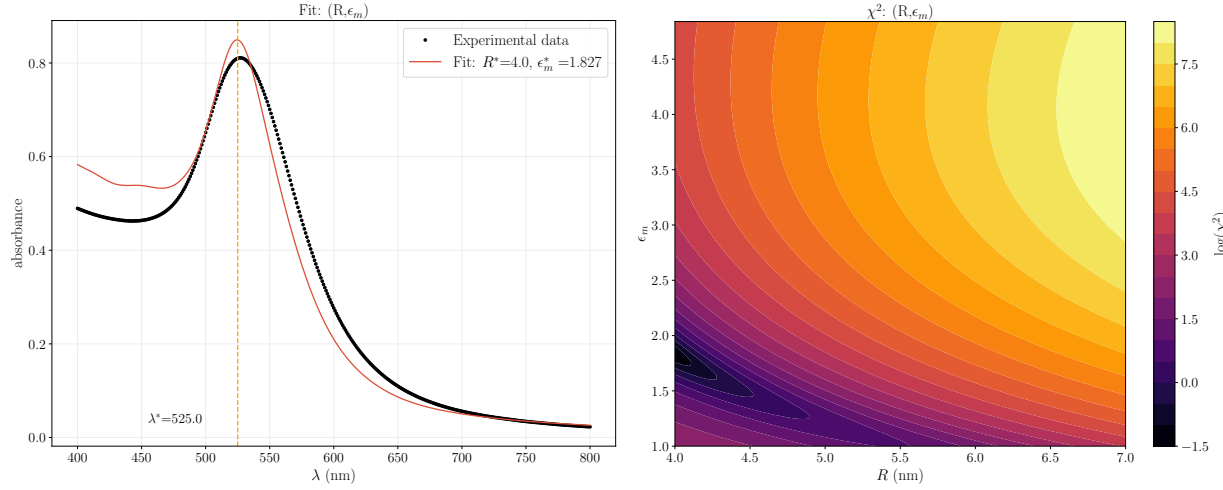


Figure 4: questo è R, rho



(a) fit

(b) χ^2 sistema il range del secondo fit! Può essere che però peggiori la stima di ϵ_{psm} Figure 5: questo è R, ϵ_{psm}

4 XRD Analysis

4.1 Method

4.2 Results

5 SEM Analysis

5.1 Method

5.2 Results

6 Conclusions

References

- [1] N. W. Ashcroft and N. D. Mermin. *Solid State Physics*. Holt-Saunders, 1976.
- [2] Charles Kittel. *Introduction to Solid State Physics*. 8th ed. Wiley, 2004. ISBN: 9780471415268.