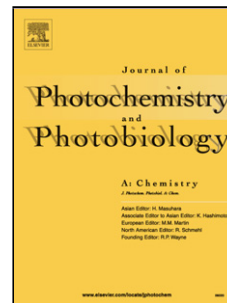


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# Photochemical synthesis: effect of UV irradiation on gold nanorods morphology

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**Abstract:** Gold nanorods (AuNRs) were synthesized by photochemical method, through irradiation of a reaction solution, containing gold precursor, surfactant and a mild reducing agent to speed up the process. The effects of the irradiation parameters on the morphology of the formed AuNRs were investigated by UV-Vis absorption spectra and transmission electron microscopy. Specifically, the control of the UV irradiance (irradiation power per unit area) and irradiation time allowed the preparation of AuNRs with a wide range of sizes. Increase of the irradiation power leads to the formation of smaller AuNRs, with concomitant decrease of length and diameter. Since both axes show a simultaneous size decrease, the produced AuNRs have increased aspect ratio. Overall we show that application of high UV irradiance for short times favors the synthesis of small AuNRs with increased anisotropy. We propose that the rise of the irradiation power primarily accelerates the reduction of the gold precursor, promoting in such way the formation of smaller seeds. Short irradiation times guard against dissolution effects on the formed nanorods.

Keywords: gold nanorods – photochemical synthesis – nucleation – anisotropic growth

## 1. Introduction:

Metallic nanoparticles have received great interest in the last decade due to their unique optical and electronic properties. Between them gold nanoparticles are possibly the most studied ones due to their remarkable properties. Indeed, numerous works deal with the synthesis and size or shape control of gold nanoparticles, studying also their properties and suitable fields of applications<sup>1-6</sup>. Gold nanorods (AuNRs) are intensively examined, mainly due to their anisotropy-dependent optical properties. AuNRs display two distinct surface plasmon resonance peaks in the visible/near-infrared spectral range, attributed to the coherent oscillation of conduction electrons along the transversal and longitudinal axes of the NRs<sup>7</sup>. The transversal mode gives rise to a resonance peak at 520 nm, called transverse surface plasmon (TSP). The longitudinal mode shows a resonance peak position sensitive to the NRs' aspect ratio (length/diameter), ranging between 600 and 800 nm, and is called longitudinal surface plasmon (LSP). Many scientific fields can benefit from the unique properties of the AuNRs, including optics<sup>8</sup>, biology (biosensors, cell imaging, drugs delivery, tissue engineering and chemotherapy)<sup>9,10</sup> and photonics<sup>11</sup>. The excitation of localized surface plasmon resonances results in the confinement of electromagnetic waves in regions below the optical diffraction limit near the metal surface. This near-field enhancement has been employed to amplify Raman scattering, fluorescence, high harmonic generation, Faraday rotation, photocurrent, photopolymerization, light absorption, and circular dichroism<sup>12-14</sup>.

The numerous application fields of AuNRs, boosted the development of several synthesis protocols. These include chemical (seed-mediated)<sup>15-18</sup>, electrochemical<sup>19</sup>, template<sup>20</sup> and photochemical synthesis<sup>21,22</sup>. Among the different strategies seed-mediated growth is undoubtedly the most popular. The photochemical protocol for the synthesis of AuNRs offers a good alternative to the seed mediated growth, overcoming the critical problem of preliminary seeds production and the long time requirement. Esumi et al worked on the AuNRs synthesis irradiating with UV light a HAuCl<sub>4</sub> solution in presence of hexadecyltrimethylammonium chloride<sup>23,24</sup>. Afterwards, Yang and co-workers implemented the photochemical method for the synthesis of AuNRs adding different amounts of silver nitrate<sup>21,25</sup>. Silver nitrate was found to facilitate the formation of AuNRs with controlled aspect ratio. In order to shorten the long times required for the synthesis Yamada and co-workers refined the synthesis protocol by combination of chemical and photochemical methods leading to an acceleration in the rate of NRs formation<sup>22</sup>. In this approach first a mild reduction of the gold precursor is induced by the addition of a small amount of ascorbic acid and subsequently reduction to Au(0) is accomplished through UV irradiation and AuNRs formed. Further reports on the AuNRs photochemical synthesis dealt mainly with the role of chemical components of the reaction solution, such as acetone<sup>26,27</sup>, silver ion<sup>25,28</sup> and ascorbic acid<sup>29</sup>, on the formation of the NRs. Ahmadi and co-workers investigated the effects of wavelength and intensity of UV light on the growth of AuNRs by photochemical reduction of HAuCl<sub>4</sub> in a micelle solution of CTAB and tetraoctylammonium bromide<sup>26</sup>. With the aim to restrict the study to the role of the UV light, the authors chose to carry the irradiation for extremely long times, on a precursor solution free from reducing agents. Under these conditions the use of UV light of 300 nm wavelength was found to be more effective in inducing formation of longer AuNRs than the wavelength of 254 nm.

Furthermore UV irradiation with higher intensity led to the increase in the concentration and in the length of the formed AuNRs. The experimental results were explained through an acceleration of the photoreduction of the gold ions, at the higher intensities of irradiation, inducing faster growth of the NRs. As an alternative technique for rapid synthesis of AuNRs, it was proposed the use of a photoinitiator as source of ketyl radicals<sup>30</sup>. Here again due to the rapid burst of ketyl radicals induced by the photoinitiator the authors avoided the use of reducing agents in the precursor solution and performed the synthesis in the absence of ascorbic acid, irradiating with UV light at 350 nm. The effect of UV radiation reported for this modified protocol is similar to the one reported in <sup>26</sup> with the exception of the shorter irradiation times.

The effects of irradiation parameters on the rapid photochemical synthesis, in the presence of ascorbic acid, and their consequences on the AuNRs morphology were only little studied until now. The precursor solution absorption changes strongly after the addition of the ascorbic acid. Specifically, addition of ascorbic acid to the precursor solution, in the rapid synthesis protocol, makes the solution instantaneously transparent and its absorption at 300 nm negligible, due to the reduction of  $\text{AuBr}_4^-$  to  $\text{AuBr}_2^-$ . Consequently, in the fast photochemical synthesis UV irradiation at wavelength 256 nm was found to be more effective for the formation of AuNRs<sup>27</sup>. We expect the oxidation state of the gold complexes in the precursor solution to be crucial also for the kinetics of the nucleation of the gold nanoparticles and of the reactions responsible for their anisotropic growth as well as for the balance between these reactions. This work aims to investigate the photochemical process for the rapid synthesis of AuNRs, focusing on the effects of UV irradiation on the formed AuNRs morphology. In the photochemical strategy the irradiation is expected to cause primarily reduction of the gold precursor through generation of ketyl radicals. The main drawback of the photochemical synthesis protocol is

limited control of the size of the NRs due to the simultaneous nucleation of the Au seeds and their growth into rods. Tuning either the power or the time of irradiation we give the insight of the competitive reactions of nucleation and growth resulting into AuNRs formation. Optical characterization and electrical microscope measurements of the synthesis outcome allow for a precise discussion of the role of UV irradiation on the morphology of the AuNRs. The results show that suitable choice of the irradiation parameters provide a significant tool to control the AuNRs morphology and aspect ratio. To the best of our knowledge this is the first investigation on the role of the irradiation on the nucleation and growth of the AuNRs, separately, in presence of ascorbic acid.

## 2. Material and methods

Hexadecyltrimethylammonium bromide CTAB (Fluka  $\geq 99.0\%$ ), hydrogen tetrachloroaurate trihydrate  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (Alfa Aesar 99.99% (metal basis), Au 49.5% min), and silver nitrate  $\text{AgNO}_3$  (Sigma Aldrich 99.9999%) were used without further purification. Ascorbic acid (99%), acetone and cyclohexane from Sigma Aldrich were used as received. All solutions were prepared using Milli-Q double distilled water (resistivity  $> 18.2 \text{ M}\Omega \cdot \text{cm}$ ).

To 3.32 mL of reaction solution, containing  $24 \times 10^{-5}$  moles of CTAB,  $0.6 \times 10^{-5}$  moles of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  and  $0.07 \times 10^{-5}$  moles of  $\text{AgNO}_3$ , were added 0.065 mL of acetone and 0.045 mL of cyclohexane. After addition of 0.2 mL of Ascorbic acid (40 mM) the color of the solution changed from deep orange to colorless, within 1 minute.

3 mL of the precursor solution was put into quartz cuvette of optical path length 1cm, and irradiated with UV light from an ultrahigh-pressure mercury argon lamp (Oriel 6035 Hg (Ar)) with narrow line at  $\lambda = 253.7 \text{ nm}$ , with 90% of the output, without stirring. The additional

spectral lines with scarce output emitted by this lamp are in the low absorption zone of the precursor solution.

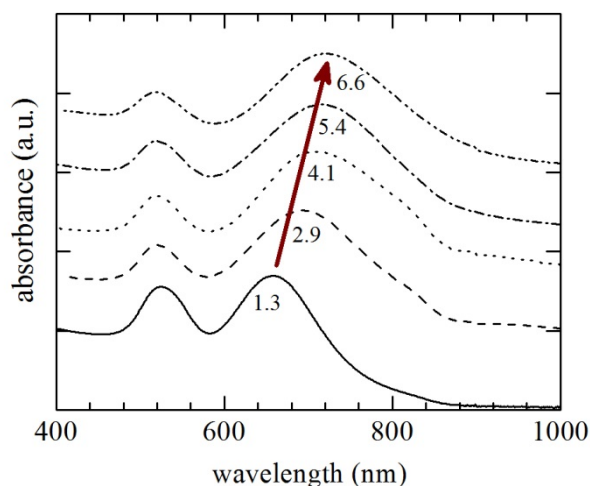
The intensity of irradiation was modified by varying the distance between the cuvette and the lamp between 1 cm and 7 cm. The power of the UV light was measured before and after irradiation of the precursor solution, by power meter Thorlab PM150. The experimental set up was covered with a black box during the irradiation to prevent any possible interaction with other light sources in the lab. For each irradiation condition, the synthesis was repeated four times and the results found reproducible with a deviation on the peak position smaller than 5 nm.

After irradiation, the reaction solution was centrifuged at 4000 rpm for 10 min to separate the big gold clusters. The resulting supernatant was collected and centrifuged at 14000 rpm for 20 min. The precipitate was collected and washed twice to discard the excess of CTAB and the unreacted materials from the solution. The supernatant was exchanged with double distilled water and the final precipitate was dispersed in 1 mL of distilled water and used for characterization. 20  $\mu$ L of NRs solution dispersed in water was deposited on carbon coated copper grid and dried under vacuum for transmission electron microscopy (TEM) investigation. The transmission electron micrographs were taken by JEOL JEM1011 at 100 KV. The statistical analysis of TEM micrograph was obtained measuring the length and the diameter of 200 AuNRs for each sample. 100  $\mu$ L of each AuNRs solution was diluted in 400  $\mu$ L double distilled water in a quartz cuvette with optical path length 2 mm for optical absorption analysis. The absorption spectra of all AuNRs solutions were collected using UV-Vis-NIR spectrophotometer Varian Cary 6000i.

### **3. Results and discussion**



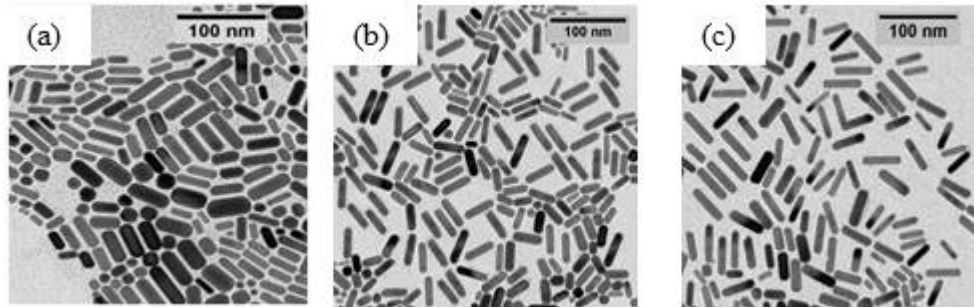
AuNRs were synthesized at different irradiances for fixed irradiation time in order to investigate the role of light power on the synthesis process. The time of irradiation was fixed to 30 min along the lines of previous experimental works on rapid AuNRs synthesis by combination of chemical reduction and photoirradiation.

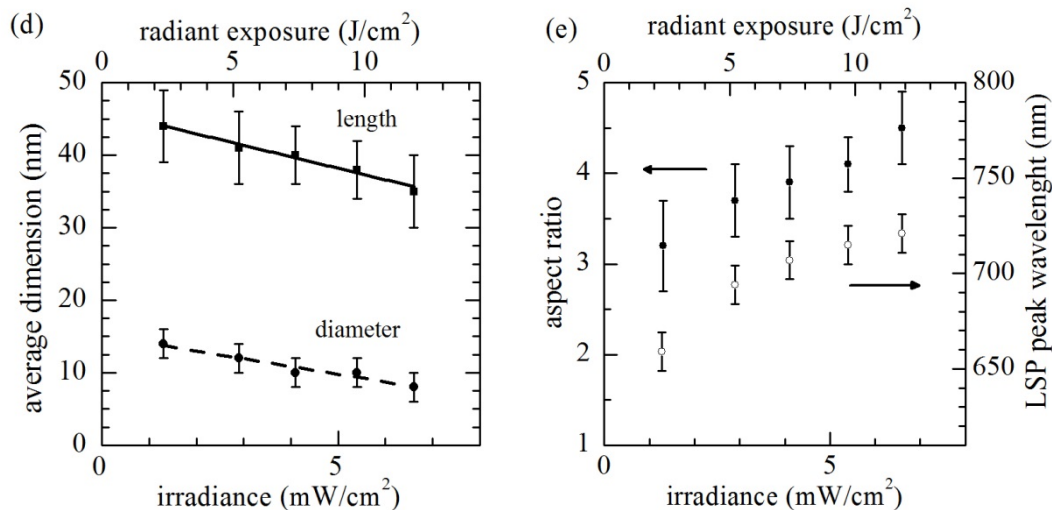


**Figure 1.** UV-Vis spectra of AuNRs synthesized at different irradiance values. Numbers next to the spectra specify the used values in  $\text{mW}/\text{cm}^2$ .

Figure 1 summarizes the optical characterization of different solutions resulting after 30 min irradiation at increasing irradiance values, from 1.3 to 6.6  $\text{mW}/\text{cm}^2$ . In the investigated range, the rise of the UV irradiance induces a red shift in the LSP absorption peak of the produced NRs. The red shift of the peak wavelength versus the used irradiance is better demonstrated in Figure 2 (e). Increasing the irradiance from 1.3 to 2.9 and then to 4.1  $\text{mW}/\text{cm}^2$  (radiant exposure range 2.3-7.4  $\text{J}/\text{cm}^2$ ) the position of the LSP peak shifts from 659 nm to 694 nm and to 708 nm, respectively. At even higher UV irradiances, 5.4  $\text{mW}/\text{cm}^2$  and 6.6  $\text{mW}/\text{cm}^2$  (corresponding to radiant exposure of 9.7 and 11.9  $\text{J}/\text{cm}^2$ ) the LSP peak shifts to 715 nm and 721 nm. The TSP absorption peak position holds steady at 520 nm for all the investigated

irradiance range. The recorded shifts of the LSP peak position with increasing irradiance indicate a gradual increase of the aspect ratio. The rate of this increase seems to be greater at the lower investigated irradiances.



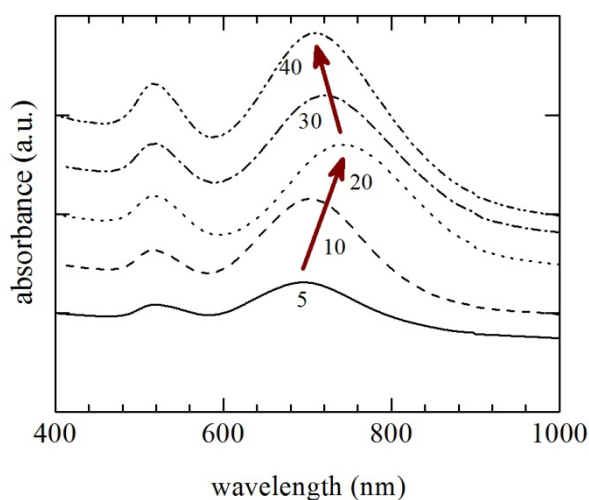


**Figure 2.** TEM micrographs of dispersed AuNRs produced after irradiation for fixed irradiation time, 30 min, at different UV irradiances, (a) 1.3 (b) 4.1 and (c) 5.4 mW/cm<sup>2</sup>. Average dimensions (length and diameter) and aspect ratio of the AuNRs versus UV irradiance, respectively (d) and (e). Lines are the linear fits of the data.

In order to identify the variations in the NRs morphology causing the recorded changes in the absorption spectra, TEM measurements were performed and are presented in Figure 2. The NRs' average dimensions and aspect ratios at the different irradiance values were evaluated by statistical analysis of the TEM images, Figure 2 (d, e). The increase of the UV irradiance is found to induce linear decrease of both NRs dimensions. In particular, increasing the irradiance from 1.3 to 6.6 mW/cm<sup>2</sup> (radiant exposure from 2.3 to 11.9 J/cm<sup>2</sup>) the AuNRs' average length linearly decreases from 44±5 nm to 35±5 nm, and the average diameter also linearly decreases from 14±3 nm to 10±2 nm, see figure 2 (d). The rates of decrease of the AuNRs dimensions, roughly estimated by the linear fits of the data, are  $-1.6 \pm 0.1 \text{ nm} \cdot \text{cm}^2/\text{mW}$  for the length and  $-1.1 \pm 0.1 \text{ nm} \cdot \text{cm}^2/\text{mW}$  for the diameter, Figure 2 (d). Therefore, increasing irradiance leads to the formation of NRs with increasing aspect ratio values, consistent with the optical absorption

results, see Figure 2 (e). Aspect ratios of the synthesized AuNRs are found to increase from 3.0, at irradiance  $1.3 \text{ mW/cm}^2$  (radiant exposure  $2.3 \text{ J/cm}^2$ ) to 4.5 at irradiance  $6.6 \text{ mW/cm}^2$  (radiant exposure  $11.9 \text{ J/cm}^2$ ).

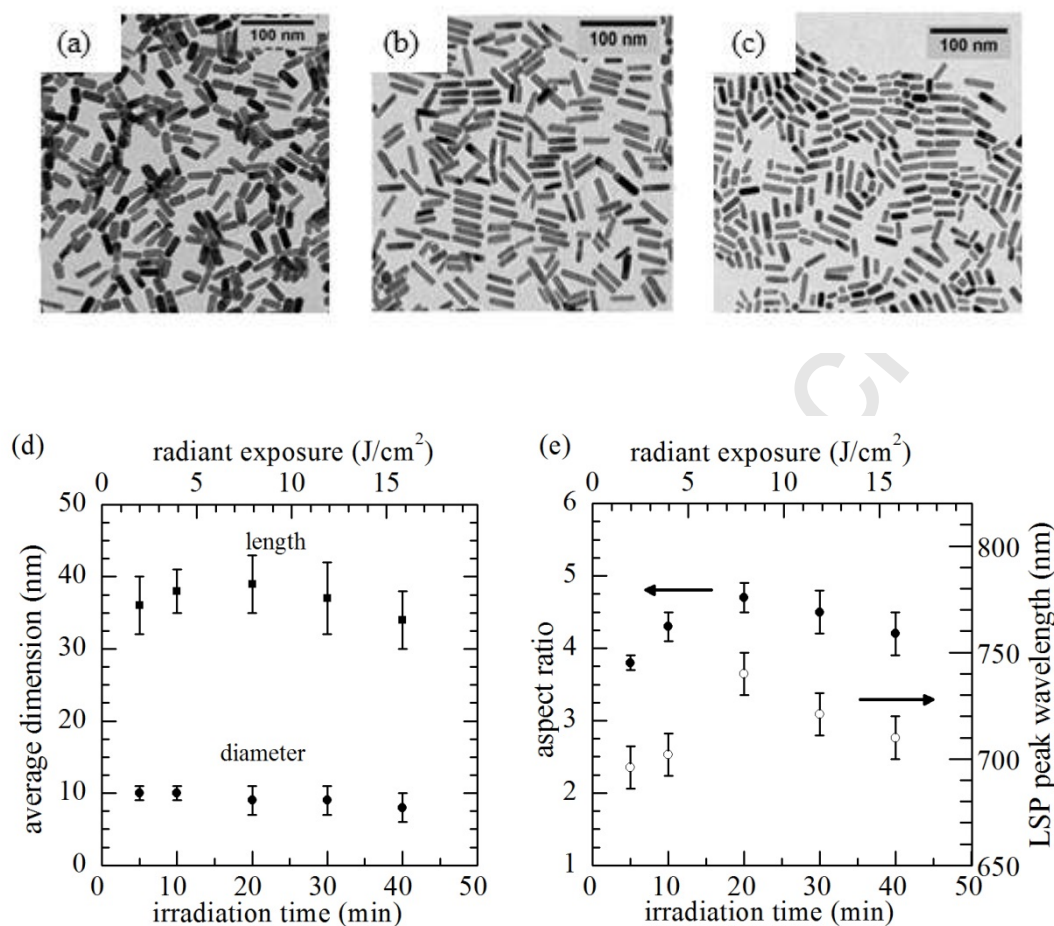
Next, we repeated the photochemical synthesis keeping stable the irradiance at the highest previously used value  $6.6 \text{ mW/cm}^2$ , which gave the NRs with the highest aspect ratio, and tuning the irradiation time from 5 to 40 min. In this way the radiant exposure range was the same as the one used in the above-presented results for different irradiation powers. The produced solutions of NRs show first a strong red shift of the LSP peak for increasing irradiation times from 5 to 20 min, followed by blue shift for 30 and 40 min of irradiation, see Figure 3.



**Figure 3.** UV-Vis spectra of AuNRs synthesized at different irradiation times. Numbers next to the spectra specify the irradiation time in min.

The LSP absorption peak shifts are connected to the AuNRs' morphological changes. In order to follow the growth of the AuNRs with the irradiation time we performed statistical

analysis using TEM images, taken at different irradiation times. During the first 20 min of irradiation, the AuNRs become gradually longer while their diameter practically remains constant, see Figure 4. Further prolongation of the irradiation leads to decrease of the length of the produced NRs, which becomes clearly noticeable after 40 min of irradiation. This decrease of the length on the produced NRs can only be attributed to dissolution of the already produced NRs, which is highly likely to happen at high irradiation powers especially when the entire precursor is already consumed during the photochemical synthesis<sup>25,26</sup>. In particular in case of lack of gold precursor, under UV irradiation AuNRs were proposed to dissolve, one by one breaking gold atoms from the AuNRs surface, in favor of more thermodynamically stable spherical nanoparticles. This ripening process is expected to be favored on the less protected AuNRs tips. Consequently overirradiation results in shortening of the formed AuNRs and simultaneous increase in fraction of the gold nanospheres. Consistently our experimental results show AuNRs shortening at the longer irradiation times, Figure 4 (a). Whereas the exceeding spherical NPs are not detected as they are separated during the centrifugation process. The choice of 30 min as irradiation time in the above-presented experiment is safe in order to restrict our study at the nucleation and growth stages of the synthesis, avoiding the drawback of over-irradiation. Although it is evident from this set of synthesis that the best result, for irradiance  $6.6 \text{ mW/cm}^2$ , is obtained reducing the time of irradiation to 20 min, this would not be the case for the lower irradiances applied in the first part of the work. In fact the irradiation time needed for the best synthesis results is different for each irradiance, mainly depending on the maximization of gold precursor consumption before over-irradiation takes place. Therefore, in the first part of the work we chose to fix the irradiation time to a value that allowed us to investigate a range of radiant exposure around the optimized value of  $8 \text{ J/cm}^2$  (20 min at  $6.6 \text{ mW/cm}^2$  irradiance).



**Figure 4.** TEM micrographs of dispersed AuNRs produced after irradiation for fixed irradiance,  $6.6 \text{ mW/cm}^2$ , at different irradiation times, (a) 5 (b) 20 and (c) 40 min. Average dimensions (length and diameter) and aspect ratio of the AuNRs (d) and (e) respectively, versus irradiation times.

In AuNRs photochemical synthesis UV irradiation is expected to induce the reduction of Au (I) ions to Au (0) through the generation of ketyl radicals via excitation of acetone and hydrogen atom abstraction from CTAB<sup>27</sup>. In the early stage of irradiation the Au (0) concentration in the reaction solution is progressively increased, by the effect of the photochemical reaction of ketones. Once the monomer concentration reaches supersaturation, above a critical radiant exposure threshold, nucleation starts and nuclei form. In the following

stage, the growth of the formed nuclei happens in parallel with further nucleation. The growth of the nanorods is accomplished by reduction of the precursor complex on the surface of the nanocrystals. This growth was proposed to be assisted and accelerated by ketyl radicals transferring electrons to the colloids, as for the photochemical synthesis of silver nanoparticles<sup>31</sup>. The anisotropic growth was shown to be ensured primary by the preferential absorption of silver ions on specific gold facets, hindering the growth on those facets<sup>32</sup>, together with the interaction of the ellipsoidal gold seeds with the cationic micelles transporting the gold ions<sup>33,34</sup>.

In the first above-presented experiment for the photochemical synthesis of AuNRs, we expect to increase the rate of formation of ketyl radicals in the reaction solution by increasing the irradiation power. Gold species reduction could then occur through one of two competitive reactions. The faster photochemical reaction of ketones can induce rapid increase of the Au (0) concentration in the reaction solution. In this case we expect irradiance rise to favor faster nucleation and therefore the formation of an increased number of smaller nuclei<sup>35</sup>. The ketyl radicals can also transfer electrons to the surface of the nanocrystals assisting the reduction of the Au precursors' complex which leads to the NRs growth. In this case increasing the irradiation power would result in faster colloids' growth and consequently in longer AuNRs. On the contrary, our experimental results point out an overall decrease of the AuNRs dimensions, with similar size lowering rate for both axes,  $-1.6 \pm 0.1 \text{ nm.cm}^2/\text{mW}$  for longitudinal dimension and  $-1.1 \pm 0.1 \text{ nm.cm}^2/\text{mW}$  for transversal one. This suggests that the predominant effect of the increase in the irradiation power is the enhancement of nucleation of small colloids. Whereas we assume that the growth of the NRs is controlled primarily by the time of irradiation, providing the precursor is not finished through photoreduction.

The presented results demonstrate that we were able to gain considerable control of the AuNRs morphology using different combinations of irradiation time and power, at similar radiant exposure values. In fact, precursor solution radiation with  $1.3 \text{ mW/cm}^2$  irradiance for 30 min ( $2.3 \text{ J/cm}^2$  radiant exposure) or with  $6.6 \text{ mW/cm}^2$  irradiance for 5 min, ( $2.0 \text{ J/cm}^2$  radiant exposure) results in AuNRs with very different morphologies. In the first case ( $1.3 \text{ mW/cm}^2$  for 30 min) the resulting AuNRs have average length of  $44 \pm 5 \text{ nm}$ , whereas in the second case ( $6.6 \text{ mW/cm}^2$  for 5 min) the produced AuNRs are quite shorter, with average length of  $36 \pm 4 \text{ nm}$ . At the same time the average diameter of the NRs is  $14 \pm 2 \text{ nm}$  and  $10 \pm 1 \text{ nm}$ , respectively. Overall synthesis with higher irradiances produces smaller AuNRs with higher aspect ratio, even if the used radiant exposure is the same.

#### 4. Conclusions

The effect of the UV irradiation on the morphology of the AuNRs produced through photochemical protocol has been investigated. The experimental results clearly stress the effect of the UV irradiation power on the photochemical synthesis of AuNRs. Differently from previous reported studies increase of the irradiation power is found to induce a concomitant decrease of both axes of the NRs, resulting in an increase of the aspect ratio. The concomitant decrease of both dimensions of the produced AuNRs is explained by faster reduction of the gold precursor and therefore higher monomer concentration during the nucleation. This last is a known condition promoting formation of smaller nuclei. Fine tuning of the power and of the irradiation time can provide a significant tool to control the AuNRs aspect ratio. In particular we propose increase of the irradiance and shortening of the irradiation time as a possible strategy for the synthesis of superfine AuNRs.



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## Highlights

We investigate the role of the different irradiation parameters in the photochemical synthesis of gold nanorods.

The irradiance used in the photochemical process is found to influence primarily the nucleation stage of the synthesis of the gold nanorods.

The control of the time of irradiation allows to follow the growth of the gold nanorods, till the precursor is finished through photoreduction.

