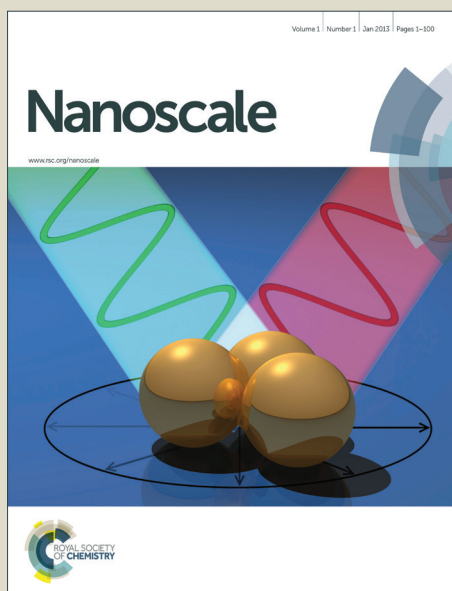


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## ARTICLE

# Drastic Nickel Ion Removal From Aqueous Solution By Curcumin-Capped Ag Nanoparticles

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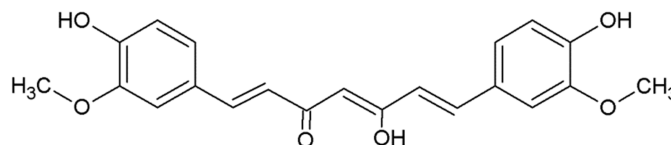
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A totally green synthesis protocol has been adopted to obtain silver nanoaggregates capped by the natural compound (1E, 6E)-1,7-Bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-diene, also known as curcumin. The synthesis process has been monitored by means of infrared, Raman, visible and fluorescence spectroscopies. Characterization confirms that curcumin reduces and caps the nanoparticles and such procedure allows its solubility in water and drastically increases the curcumin stability. Silver nanoparticles (AgNPs)/curcumin complex has been dispersed in a water solution containing a known nickel ion concentration. After three days a grey precipitate is observed and the nickel concentration in the solution is reduced of about 70%.

## Introduction

Nickel is present in the environment in small quantities (about 6-20 ng m<sup>-3</sup>) and it is used in jewellery industry and in the metallic alloys production. As reported for many heavy metal elements<sup>1, 2, 3</sup> the main effects on human health are induced when they are present in the ionic form. Ni<sup>2+</sup> can be easily ingested with water or foodstuff. In fact, foodstuff ever contains quantities of nickel that is employed in the transmission of genetic code (DNA, RNA); on the contrary, when the uptake is too high, it can result very dangerous.<sup>4, 5</sup> In particular, food industry pays great interest towards the control of nickel concentration in the foodstuff since it induces, in particular subjects, dermatitis, intestinal and stomach pain, chronic headache and nausea.<sup>6, 7</sup> In many countries it is forbidden to report the label Nickel Free on foodstuff because there is not a procedure able to remove nickel. It is worth to report that about 15-20% of the world's population is affected by the so-called systemic allergy syndrome (SNAS). Methods for nickel removal are reported based on bacterial biosorption ability,<sup>8</sup> chelating substances,<sup>9</sup> or iron nanostructures able to form a surface complex and reduce nickel ions to metallic nickel.<sup>10</sup> In the present work silver nanoparticles have been used as health friendly substrate<sup>11, 12, 13</sup> for curcumin molecules. Curcumin (scheme 1), extracted from turmeric, is a well-known anti-inflammatory drug<sup>14</sup> and anticancer agent,<sup>15</sup> furthermore it is able to chelate and remove nickel from aqueous solutions.



Scheme 1. Chemical structure of curcumin in its enol form.

Nickel chelation by curcuminoids is a well-known process, and it needs an alkaline pH to induce the formation of nickel square planar complexes with two curcumin molecules.<sup>4</sup> Of course, a too high pH can represent a huge problem since it can induce harmful effects on foodstuff or drinking water; in addition the curcumin extract is low soluble in water<sup>16</sup> and its stability is restricted to a few hours.<sup>17</sup> The reported issues have been overcome realizing a supramolecular blend of curcumin and silver nanoparticles.

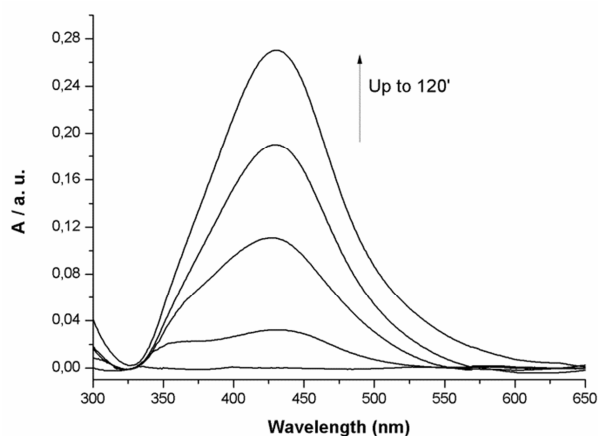
## Materials and methods

Curcumin, ferulic acid, guaiacol, NiCl<sub>2</sub> and AgNO<sub>3</sub> were purchased from Sigma and were used without further purification.

MilliQ grade water was used during synthesis and to prepare nickel contaminated samples. UV-Visible spectra were carried out by an Agilent Cary 5000 and a Fluorolog Horiba was used for photoluminescence measurements. Infrared spectra were recorded by a Perkin Elmer Spectrum One Fourier Transform spectrophotometer with an ATR plate. AFM characterization was obtained by a NanoSurf SPM S200 microscope.

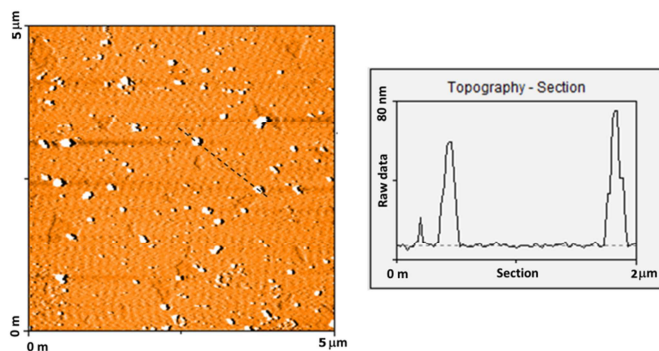
## Results and discussion

Silver nanoparticles were obtained by a simple, green and cheap procedure.  $\text{AgNO}_3$  ( $10^{-5}$  M) was dissolved in ultrapure milliQ grade water and mixed with a  $10^{-3}$  M curcumin solution. In order to dissolve curcumin (otherwise insoluble in water) it was first dissolved in a drop of ethanol and this was then dispersed in ultrapure water. The  $\text{AgNO}_3$  mixed with curcumin solution was placed in a ventilated oven at a temperature of 363 K. An aliquot of the prepared solution was withdrawn during the heating and the UV-Visible spectra were acquired. A plasmonic peak appeared at 425 nm and it increased during the time with a maximum value obtained after 120 min. In figure 1 the absorption spectra of silver nanoparticles and curcumin adducts (hereafter indicated as AgNPs/curcumin) are reported and the maximum absorption appears to be 5 nm blue shifted if compared with the curcumin absorption peak. Signal appeared very broad, suggesting the presence of large aggregates and a mixture of nanostructures with different shapes.<sup>18</sup>



**Figure 1.** Spectroscopic evidence of the formation of silver plasmonic peak during the synthesis.

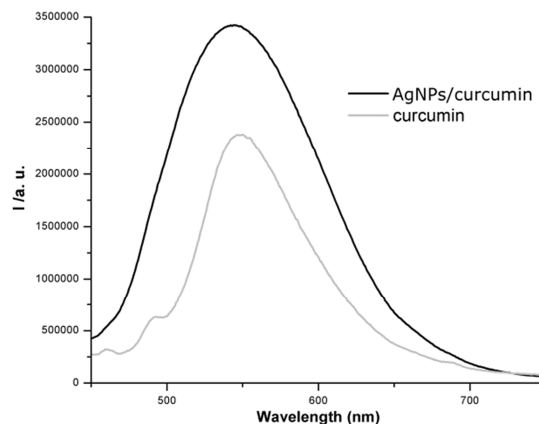
The aggregates were morphologically characterized by means of AFM (figure 2), confirming the presence of large domains with different dimensions.



**Figure 2.** AFM image of a cast film of AgNPs/curcumin complex on silicon substrate. As reported in the picture, the aggregate dimensions range from 120 to 230 nm.

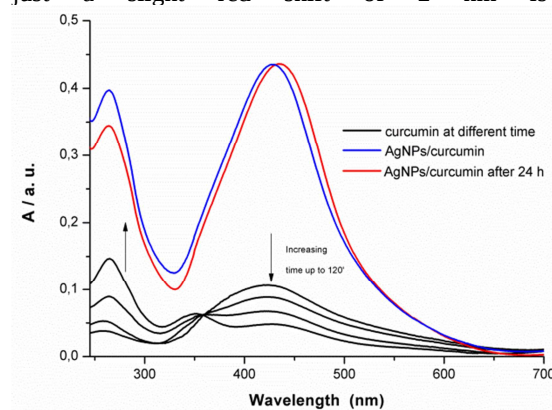
Fluorescence emission of curcumin dissolved according to the previously reported procedure, obtained exciting at 430 nm,

showed a broad band with a maximum emission at 550 nm, and the spectral profile appeared unchanged when AgNPs/curcumin are formed (figure 3). An increase of fluorescence emission is induced by the presence of silver nanoparticles.



**Figure 3.** Fluorescence emission of curcumin and AgNPs/curcumin obtained with an excitation wavelength of 430 nm.

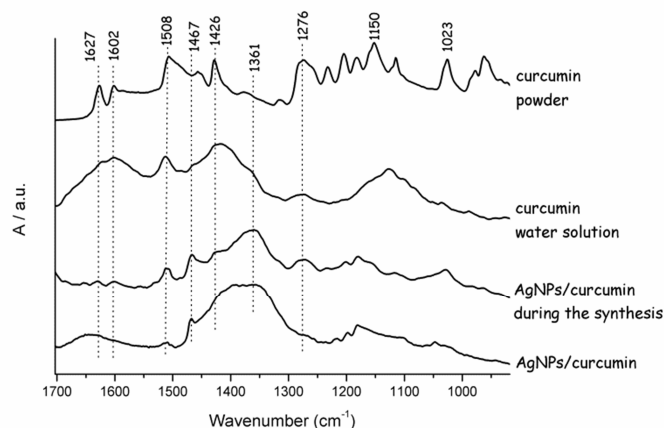
As reported in figure S1 of the ESI, the degradation products of curcumin, i.e. ferulic acid, vaniline and feruloylmethane,<sup>19</sup> showed weak fluorescence emission with different spectral profiles. It suggests that such a procedure preserves the chemical structure of curcumin allowing its solubility and stabilization in water. Stability of AgNPs/curcumin at room temperature was compared with the degradation pathway of pure curcumin in the same conditions. As reported in figure 4, curcumin visible spectrum strongly change during 120 min: the absorption band of vaniline at 265 nm increases and the curcumin peak at 425 nm monotonically decreases. The complex AgNPs/curcumin appears stable up to 24 hours and just a slight red shift of 2 nm is recorded.



**Figure 4.** Curcumin degradation at room temperature during 120 min (black spectra) and stability of the dispersion AgNPs/curcumin in 24 hours (blue and red lines).

Such a result can be of paramount importance in many fields: curcumin has been proposed in biomedical and biotechnology applications but a crucial problem with such a compound is related to its low stability that strongly affects its properties.

In order to better understand the synthesis process, the procedure was repeated substituting curcumin with its degradation products: vaniline and ferulic acid (see supporting information). Only ferulic acid was able to reduce the silver ion to metallic form, even if it needed 6 hours; therefore pristine curcumin molecule appears to be crucial for AgNPs formation. Infrared spectroscopy was used to understand the reduction and capping mechanism that takes place during the AgNPs/curcumin adduct generation (figure 5).



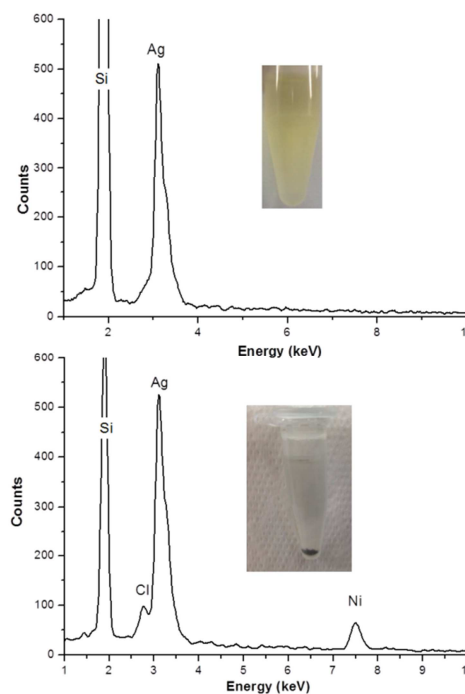
**Figure 5.** FTIR spectra of curcumin powder (SIGMA), curcumin water solution, AgNPs/curcumin during the synthesis and AgNPs/curcumin after synthesis.

FTIR spectrum of curcumin standard powder was recorded and is shown in figure 5. The peak at  $1627\text{ cm}^{-1}$  is due to a contemporaneous contribution of C=C and C=O stretching mode, whilst the peak at  $1602\text{ cm}^{-1}$  corresponds to the C=C stretching vibration of the aromatic ring.<sup>20, 21</sup> The signal at  $1508\text{ cm}^{-1}$  should derive from superimposition of  $\nu(\text{C}=\text{C}_{\text{ring}})$  and  $\nu(\text{C}=\text{O})$  vibrations.<sup>20, 21</sup> The  $1500\text{--}1350\text{ cm}^{-1}$  range, characterized by the presence of the absorption peaks at  $1456\text{ cm}^{-1}$ ,  $1426\text{ cm}^{-1}$  and  $1373\text{ cm}^{-1}$ , is the region of the in-plane bending vibrations of C-H, skeletal CCC and aromatic CCC and CCH modes.<sup>20, 22</sup> The strong peak at  $1276\text{ cm}^{-1}$ , instead, can be assigned to the  $\nu(\text{C}-\text{O})$  of the enol function.<sup>21</sup> The other C-O-C stretching and out of plane bending of  $\text{CH}_3$ , together with in plane bending of aromatic CCH bands are apparent at the  $1250\text{--}900\text{ cm}^{-1}$  region of the spectrum.<sup>20</sup>

An ultrapure water solution of curcumin was prepared, according to the previous procedure, and the IR spectrum was recorded (figure 5), in order to confirm that hydration does not strongly affect the principal absorption peaks of the natural compound. A general broadening of all the principal peaks is observed, but frequencies remain almost unchanged.

By analyzing the IR spectra of AgNPs/curcumin during and at the end of the synthesis, we confirmed that the keto-enol group of the molecule act both as reducing agent for the silver nitrate and as capping site. The intensity of the involved atomic group vibration modes strongly decreases in the spectra shown in figure 5. In particular the signals at  $1627\text{ cm}^{-1}$  and  $1272\text{ cm}^{-1}$ , due respectively to carbonyl stretching mode and C-O stretching of the enol, disappear, being probably bound to silver. Therefore, the lack of the signals at  $1602\text{ cm}^{-1}$  ( $\nu(\text{C}=\text{C}_{\text{ring}})$ ) and the intensity decrease of signals at around  $1025\text{ cm}^{-1}$  (out of plane bending of aromatic CCH) suggested that also the aromatic rings are interacting with the metal. Finally the presence of the signals at  $1467\text{ cm}^{-1}$ ,  $1426\text{ cm}^{-1}$  and  $1361$

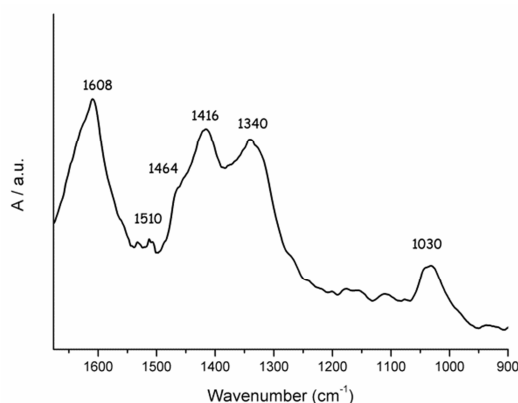
$\text{cm}^{-1}$ , involving the olefin in plane bending vibrations of the heptadiene chain, confirmed the presence of intact curcumin moiety, as already reported for gold nanoparticles capped by curcumin.<sup>22</sup> A schematic representation of the Ag capped nanoaggregates is reported in figure S3 of ESI file. The colloidal suspension of AgNPs/curcumin was dispersed in a cuvette containing nickel chloride in ultrapure milliQ grade water with a final  $\text{Ni}^{2+}$  concentration of  $1\text{ mM}$  and, simultaneously, in a cuvette of ultrapure water. Just after one day from the injection, an abundant precipitate is clearly evident in the presence of nickel ions, and after five days the solution appears transparent at the naked eye (see inset in figure 6) and no absorption band in the visible range is detectable. It can be supposed that the complex AgNPs/curcumin chelates the nickel ions and the new aggregate, probably with a lower solubility in water, precipitates. In this context, Energy Dispersive Spectroscopy (EDS) SEM elemental analysis measurements on the pellet of AgNPs/curcumin and  $\text{Ni}^{2+}$  suspension and the pellet obtained by centrifugation of AgNPs/curcumin have been carried out. In both spectra, a signal imputable to silver absorption is evident at  $3.1\text{ keV}$ , and in the pellet of  $\text{Ni}^{2+}$  contaminated dispersion a strong signal at  $7.5\text{ keV}$  is undoubtedly imputable to nickel. It is worth to observe that nickel and chloride ( $2.7\text{ keV}$ ) are in a stoichiometric ratio of  $1:0.6$ , suggesting that nickel ions are chelated.



**Figure 6.** Energy dispersive spectrometry of the pellet obtained from Ag/curcumin (extracted by centrifugation) and leaching of Ag/curcumin in presence of nickel ions. Signal at  $3.1\text{ keV}$ , related to silver are evident in both spectra. In the box below, the precipitate from AgNPs/curcumin contaminated with  $\text{Ni}^{2+}$  suspension shows an evident nickel signal. In the inset of the two images, the Eppendorf containing AgNPs/curcumin and AgNPs/curcumin contaminated with nickel after 3 days are reported: strong chromatic differences, clearly notable even by naked eyes, are evident.

Finally, the effective removal of nickel from the aqueous solution has been monitored by means of the well-known dimethylglyoxime test for nickel quantification. An aqueous solution containing  $\text{NiCl}_2$  (2 mM) has been mixed with AgNPs/curcumin dispersion in a volume ratio 1:1 (final nickel concentration 1 mM). After 3 days the  $\text{Ni}^{2+}$  concentration was calculated by dimethylglyoxime test<sup>23</sup> and a concentration of nickel ions of  $(0.3 \pm 0.02)$  mM has been obtained, with a diminution of the nickel concentration of about 70%.

The nickel binding mechanism was deeply studied by FTIR ATR spectroscopy. The FTIR spectrum of the obtained pellet is reported in figure 7.



**Figure 7.** FTIR spectrum of the precipitate obtained after 3 days when  $\text{NiCl}_2$  was mixed in a volume ratio 1:1 (final nickel concentration 1 mM) with AgNPs/curcumin.

In the recorded infrared spectrum, signals at  $1608\text{ cm}^{-1}$ ,  $1510\text{ cm}^{-1}$ ,  $1464\text{ cm}^{-1}$ ,  $1416\text{ cm}^{-1}$ ,  $1340\text{ cm}^{-1}$  and  $1030\text{ cm}^{-1}$  are apparent, confirming that curcumin is precipitated and is interacting with Ni ions, with the keto-enol function. On the other hand the heptadiene moiety remains intact. Curcumin affinity towards nickel is presumably stronger than that towards silver. Ni ions should remove Ag from the complex. Such a hypothesis seems to be confirmed by the presence of the two peaks at  $1608\text{ cm}^{-1}$  and  $1030\text{ cm}^{-1}$  due to aromatic rings vibration modes. The aromatic functions do not seem to participate in the Ni-curcumin complex formation (see figure S3 in the ESI file). The complex probably is not enough water soluble, leaching together to the released metallic Ag.

## Conclusions

Curcumin was used as reducing agent for the formation of silver nanoparticles by means of a very simple and totally green synthesis process. Fluorescence and infrared spectroscopy pointed out that curcumin capped the AgNPs generating a very stable complex that was observed by atomic force microscopy. The AgNPs/curcumin colloidal suspension was dispersed in an aqueous solution containing nickel ions, and it was observed that in few days a dark grey precipitate was obtained only in presence of nickel in solution. Elemental analysis underlined the presence of nickel and chloride in a ratio 1:06, suggesting that the AgNPs/curcumin complex chelate the nickel ions. The presence of nickel in the supernatant was reduced by the proposed procedure of about 70%, thus proposing this path as a powerful tool for removing nickel in many foodstuff and potable water. Finally, the nickel binding mechanism by the

AgNPs/curcumin system was clarified by FTIR ATR spectroscopy. Ni ions seem to have larger affinity for curcumin than Ag ions. So the formation of  $\text{Ni}^{2+}$ -curcumin complexes induced the metallic Ag release. Both the complex and the reduced silver precipitated, allowing the removal of the undesired metal from the water solution.

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## Notes and references

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