STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LII, 1, 2007

Dedicated to Professor Ionel Haiduc, President of The Romanian Academy at his 70th anniversary

LYSINE MEDIATED ASSEMBLY OF GOLD NANOPARTICLES

OSSI HOROVITZ[1], AURORA MOCANU[1], GHEORGHE TOMOAIA[2], LIVIU BOBOS[1], DIANA DUBERT[1], IULIA DAIAN[1], TRAIANOS YUSANIS[3] AND MARIA TOMOAIA-COTISEL[1]

ABSTRACT. This paper reports the data of an investigation of the gold nanoparticles assembly mediated by organic molecules, such as lysine. Gold nanoparticles were synthesized in citrate aqueous solution and characterized by UV-Vis spectroscopy and a strong absorption band at 528 nm is found for surface plasmon resonance. Transmission electron microscopy (TEM) images indicate a mean gold nanoparticle size of about 14 nm. The aqueous colloidal gold solution is stable in time, indicating a good electrostatic stabilization of gold nanoparticles through the adsorbed monolayer of citrate anions on nanoparticle surface. The interaction between the citrate capped gold nanoparticles in aqueous solution and lysine was investigated monitoring their UV-Vis spectra. At a certain lysine/gold ratio a new, large absorption band appears between 600 and 700 nm, which increases in time, while the color of the colloidal gold solution changes from red to blue. The 528 nm band decreases, as a consequence of the assembly formation of gold nanoparticles mediated by lysine. The nanostructure of the lysine mediated assembly of gold particles is analyzed by TEM and atomic force microscopy (AFM). The TEM and AFM images evidence the assembly of gold nanoparticles, where particles are not in direct physical contact. This effect could be explained primarily through the zwitterion-type electrostatic interactions between the charged amine and acid groups of the lysine molecules adsorbed and bound to different gold nanoparticles. These findings provide new insights into the precise control of interfacial interactions between organic molecules anchored on gold nanoparticles.

Keywords: *gold nanoparticles, lysine, self-assembly, UV-Vis spectra, TEM, AFM.*

Introduction

One of the problems which has attracted the attention of both science and industry is the integration of nanoparticles and organic molecules, in order to develop new materials for electronics and optics and new applications in biomedical and bioanalytical areas, such as controlled drug delivery, medical diagnosis devices and biosensors [1-6].

Amino acids are a promising class of organic compounds to be used in biofunctionalization of gold nanoparticles, as protective layers and for their

[1] Babes-Bolyai University of Cluj-Napoca, Faculty for Chemistry and Chemical Engineering, 400028 Cluj-Napoca, Romania,
[2] Iuliu Hatieganu University of Medicine and Pharmacy, Department of Orthopedic Surgery, 400015 Cluj-Napoca, Romania,
[3] Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece

assembly. Functional groups such as -SH and $-NH_2$ present a high affinity for gold, and since amino acids contain some of these groups, they are expected to stabilise gold nanoparticles. Their capacity of generating structural diversity was recognised [7], and gold surfaces capped with amino acids are considered to represent the simplest mimics for protein surfaces [8]. However, there are relatively few reports in the literature on surface modifications of gold nanoparticles with amino acid molecules [9–14], but no systematic study of amino acid interactions with gold nanoparticles is available.

Amino acids can be used in the assembly formation of inorganic nanoparticles. If such molecules are adsorbed and bonded to the nanoparticle surface, amino acids belonging to two different nanoparticles can be connected through a condensation reaction with peptide bonding formation, thus leading to a peptide-linked assembly of nanoparticles. The properties of such assemblies could be designed rationally by choosing the initial amino acid.

Alternatively, amino acids can be adsorbed on the metallic particle surface already during the formation of nanoparticles, using the amino acid itself as reduction agent [14-18], or latter, by ligand exchange reactions or binding on the former adsorbed stabilising molecules. In this way protecting homogeneous or heterogeneous, mixed monolayers of metallic nanoparticles can be obtained.

In our previous work, we synthesized gold nanoparticles in aqueous solutions of citrate and used them to be functionalized with biomolecules, such as protein extracted from aleurone cells of barley [19]. How citrate anions, capping agents of gold nanoparticles, are involved in the interaction between gold nanoparticles and amino acids and how colloidal solution pH influences the nanoparticle assembly are questions to be answered.

The aim of this investigation is to gain insights into the assembly formation of gold nanoparticles and interparticle interactions in the presence of lysine, which could have potential application for the analytical detection of amino acids found in various media. The investigation of the effect of lysine concentrations on the surface plasmon resonance (SPR) band evolution of gold nanoparticles is examined to describe the lysine effect on electrostatic interactions and on interparticle binding properties. The results provide important information on the affinity of gold nanoparticles to lysine molecules and its optical applications.

Lysine (three-letter code: Lys or one-letter code: K) is an amino acid with a ε-amine group on the side chain (Fig.1). It is a basic, positively charged, polar amino acid, with hydrophilic properties [20]. Its pK_a values are: 2.20 (for the carboxylic group), 9.20 (for the α-amine group) 10.1 (for the ε-amine group); and the isoelectric pH is about 9.65. Therefore, lysine is a monocationic molecule in a large interval of pH from about 4 to almost 8.

H_2N

The understanding
presence of lysine, where bo
could be operative in the
important focus in this invest

Experimental part

An aqueous colloi
reduction with sodium citr
adapted from [19, 21]. De
used in all experiments
purification system. A 200
vigorously was refluxed. T
($Na_3C_6H_5O_7 \cdot 2H_2O$), solved i
color change, the heat was
overnight to room temper
solution (c_{Au}) is 25 mg/
nanoparticles was stored in

Solid L-lysine was p
purification. Lysine was diss

The UV/Vis absorpti
Jasco UV/Vis V-530 spect
cuvettes in the 190 – 900 nr

The molar concent
experiments were the follow

The investigated mixt
(c_{Au}) and the lysine solutions
amounts of the previous mixt
solution. The gold and lysine
used in most of the determina

The gold nanoparti
presence of lysine was air-d
transmission electron micr

–NH_2 present a high affinity for
hese groups, they are expected
f generating structural diversity
pped with amino acids are
r protein surfaces [8]. However,
n surface modifications of gold
4], but no systematic study of
is available.
sembly formation of inorganic
and bonded to the nanoparticle
nanoparticles can be connected
nding formation, thus leading to
properties of such assemblies
al amino acid.
orbed on the metallic particle
particles, using the amino acid
ligand exchange reactions or
lecules. In this way protecting
ayers of metallic nanoparticles

gold nanoparticles in aqueous
ctionalized with biomolecules,
ls of barley [19]. How citrate
are involved in the interaction
and how colloidal solution pH
stions to be answered.
in insights into the assembly
rparticle interactions in the
l application for the analytical
edia. The investigation of the
e plasmon resonance (SPR)
mined to describe the lysine
terparticle binding properties.
n on the affinity of gold
al applications.
tter code: K) is an amino acid
t is a basic, positively charged,
0]. Its pK_a values are: 2.20 (for
group) 10.1 (for the ε-amine
9.65. Therefore, lysine is a
from about 4 to almost 8.

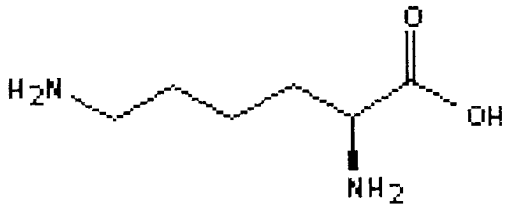


Fig.1. Lysine formula

The understanding of the gold interparticle binding properties, in the presence of lysine, where both hydrogen bonding and electrostatic interactions could be operative in the assembly process of gold nanoparticles, is an important focus in this investigation.

Experimental part

An aqueous colloidal gold solution was prepared by $HAuCl_4$ reduction with sodium citrate, in variants of the Turkevich method, as adapted from [19, 21]. Deionized water with resistivity of 18 MΩ·cm was used in all experiments and it was obtained from an Elgastat water purification system. A 200 mL 0.005% (w/w) $HAuCl_4 \cdot 3H_2O$ solution stirred vigorously was refluxed. To the boiling solution 15.3 mg trisodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), solved in a minimum amount of water, was added. After color change, the heat was turned off and the solution was allowed to cool overnight to room temperature. The gold content in the final colloidal solution (c_{Au}) is 25 mg/L. The resulting solution of colloidal gold nanoparticles was stored in a brown bottle and kept at 4 °C.

Solid L-lysine was purchased from Sigma and used without further purification. Lysine was dissolved in deionized water.

The UV/Vis absorption spectrum of all solutions was studied using a Jasco UV/Vis V-530 spectrophotometer with 10 mm path length quartz cuvettes in the 190 – 900 nm wavelengths range.

The molar concentrations (c_K) of lysine solutions used in the experiments were the following: 0.01, 0.10 and 0.54.

The investigated mixtures were obtained from the gold colloidal solution (c_{Au}) and the lysine solutions (concentration c_K), by successive removal of small amounts of the previous mixture and the adding of equal amounts of amino acid solution. The gold and lysine contents in the resulting mixtures and their ratios, used in most of the determinations, are given in Table 1.

The gold nanoparticles suspension in the absence and in the presence of lysine was air-dried on the specimen grid and observed with a transmission electron microscope (TEM: JEOL – JEM 1010). TEM

specimens consist of carbon or collodion coated copper grids. TEM images have been recorded with a JEOL standard software.

Table 1.

Gold / lysine ratios in the investigated mixtures. The concentration of the colloidal gold solution is c_{Au}; the concentration of the lysine solution is c_K.

Gold content reported to c_{Au}	Lysine content reported to c_K	Content Au/K ratio reported to (c_{Au}/c_K)
0.833	0.167	5 / 1
0.695	0.306	2.2 / 1
0.579	0.421	1.4 / 1
0.483	0.518	1 / 1.1
0.402	0.598	1 / 1.5
0.335	0.665	1 / 2
0.322	0.679	1 /2.1
0.214	0.786	1 / 3.7

Atomic force microscopy (AFM) investigations were executed on the gold nanostructured films without and with lysine using a commercial AFM JEOL 4210 equipment with a 10 x 10 (x-y) μm scanner operating in tapping (noted *ac*) mode on thin ordered gold adsorbed films on glass plates, that are optically polished and silanized with 3-aminopropyl-trietoxysilane or are prior treated to be positively charged. Standard cantilevers, non-contact conical shaped of silicon nitride coated with aluminum, were used. The tip was on a cantilever with a resonant frequency in the range of 200 - 300 kHz and with a spring constant of 17.5 N/m. AFM observations were repeated on different areas from 30 x 30 μm^2 to 250 x 250 nm^2 of the same gold film. The images were obtained from at least ten macroscopically separated areas on each sample.

All images were processed using the standard procedures for AFM. The sizes of nanoparticles were measured directly from AFM 2D-topographic images and their 3D-views. The thickness (vertical distance) variations were estimated from vertical linear cross sections and height distributions on AFM images [22-26]. AFM images consist of multiple scans displaced laterally from each other in y direction with 512 x 512 pixels. Low pass filtering was performed to remove the statistical noise without to loose the features of the sample. All AFM experiments were carried out under ambient laboratory conditions (about 20 °C) as previously reported [23, 25].

Results and discussion

Characterization of the colloidal gold solution.

The size of the colloid gold particles has been measured by TEM imaging. Two representative TEM images of these gold particles are shown in Fig.2. The particles show mostly spherical or elliptical (ovaliform) shape,

just a few triangles, penta
of a great number of parti
size (diameter) of about 1
calculated as well as the

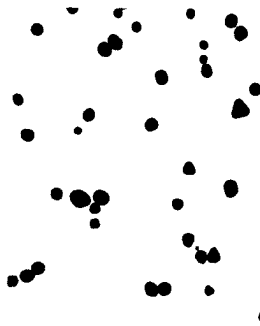


Fig.2. T

From these, the approxim
spherical) is estimated as
$8.8 \cdot 10^4$ and the number of

The visible absorpti
presents a well-defined abs
nm (Fig. 3). This value is ch
gold particles. The wavele
after preparation.

Thus, the colloidal
without observable modific
preparation. This indicate
adsorbed on the surface of
negatively charged.

Interactions of the c

The UV-Vis spectr
bands in the range of wave

The adding of a dilut
little modification in the UV-
the lowering of the absorba
absorption maxima are light
due to the changes in the d
on the gold nanoparticles su

ed copper grids. TEM images
vare.

Table 1.
he concentration of the colloidal
ation of the lysine solution is c_K.

	Content Au/K ratio reported to (c_{Au}/c_K)
	5 / 1
	2.2 / 1
	1.4 / 1
	1 / 1.1
	1 / 1.5
	1 / 2
	1 /2.1
	1 / 3.7

gations were executed on the
using a commercial AFM JEOL
operating in tapping (noted *ac*)
glass plates, that are optically
ysilane or are prior treated to be
ntact conical shaped of silicon
tip was on a cantilever with a
z and with a spring constant of
ifferent areas from 30 x 30 μm^2
ges were obtained from at least
mple.
standard procedures for AFM.
ctly from AFM 2D-topographic
tical distance) variations were
d height distributions on AFM
scans displaced laterally from
xels. Low pass filtering was
hout to loose the features of
carried out under ambient
sly reported [23, 25].

olution.
has been measured by TEM
nese gold particles are shown
or elliptical (ovaliform) shape,

just a few triangles, pentagons or hexagons are observed. From the sizes of a great number of particles, measured on the TEM images, an average size (diameter) of about 14.2 nm with a standard deviation of 2.6 nm were calculated as well as the extreme values of the sizes, from 8.5 to 24 nm.

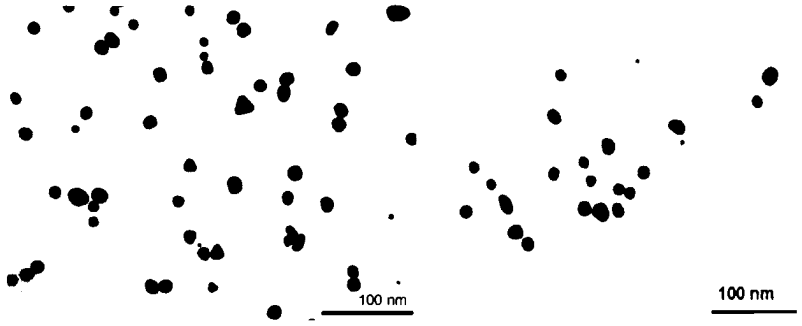


Fig.2. TEM images of gold nanoparticles

From these, the approximate average mass of a nanoparticle (considered spherical) is estimated as $2.9 \cdot 10^{-17}$ g, the number of gold atoms in a particle $8.8 \cdot 10^4$ and the number of particles per cm^3 of solution: $8.6 \cdot 10^{11}$.

The visible absorption spectra of the aqueous colloidal gold solution presents a well-defined absorption maxima at the wavelength $\lambda_{max} = 528 - 529$ nm (Fig. 3). This value is characteristic for plasmon absorbance for nanometric gold particles. The wavelength was not significantly modified during a year after preparation.

Thus, the colloidal gold solution proved to be very stable in time, without observable modifications in the UV-Vis spectrum for a year after preparation. This indicates electrostatic stabilization via citrate anions adsorbed on the surface of gold nanoparticles and the gold nanoparticles are negatively charged.

Interactions of the colloidal gold with lysine.

The UV-Vis spectrum of lysine solutions presents no absorption bands in the range of wavelengths investigated here.

The adding of a diluted 0.01 M lysine solution (Fig. 3a) produces no or little modification in the UV-Vis spectrum of the colloidal gold solution. Besides the lowering of the absorbance due to the dilution of the gold solution, the absorption maxima are lightly shifted towards longer wavelength. This shift is due to the changes in the dielectric constant in the adsorption layer anchored on the gold nanoparticles surface. This effect, probably, is due to an increase

of the average refractive index of the environment surrounding the gold nanoparticles and to the size increase of particles by the adsorbed layer.

For a more concentrated lysine 0.1 M solution (Fig. 3b) the shift towards higher wavelengths is much more important. For higher quantities of lysine added to the colloidal gold solution the SPR band becomes substantially larger, suggesting an increasing assembly formation of gold nanoparticles.

Thus, these data (Fig. 3b) show the appearance of the broad peak at longer wavelengths in the UV-Vis spectrum. This fact results from the coupling of surface plasmon resonance of two adjacent nanoparticles. This finding is an indication of the anisotropic optical properties of the gold nanoparticles self-assembled or aggregated in agreement with other published data on related systems [27].

With a very concentrated (0.54 M) lysine solution, the band for the assembly formation of gold nanoparticles mediated by lysine appears at once (maximum at about 634 nm, Fig. 3c), while the 529 nm band for individual gold particles decreases and appears only as a shoulder in the spectrum. The maximum of the broad absorption band continues its shift towards higher wavelengths in time (Fig. 3c).

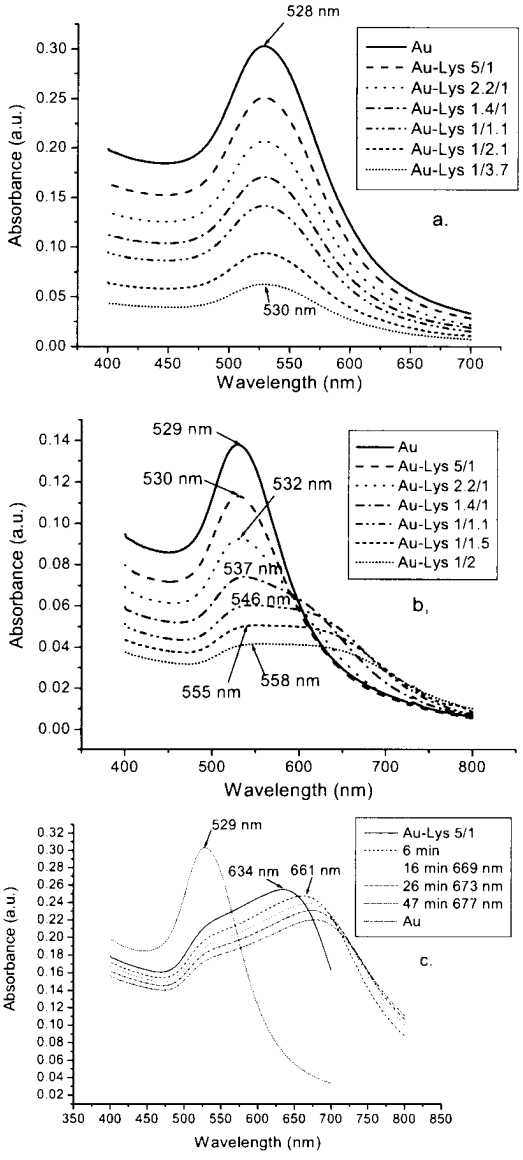


Fig. 3. Optical spectrum of colloidal gold solution with added 0.01 M (a) and 0.1 M (b) lysine solution at different ratios, and with 0.54 M lysine solution in time (c).

The color of the so
of color change is cons
aggregation phenomenon
assemblies or aggregate
nanoparticle diameter, t
coupling between the pl
bathochromic shift of the a

Lysine adsorption c
using 13 nm diameter gol
about 10.7. The UV-Vis sp
that found for citrate coa
results, using the most d
agent, the authors [30] obs
formation of peptide bonc
different gold nanoparticles
nanoparticles was shifted
633 nm. For this situation,
high concentrations of the
of gold nanoparticles media

TEM images for gol
4) show both linearly
arrangements. Finally, the
assembly of gold nanopa
evidenced by AFM observa

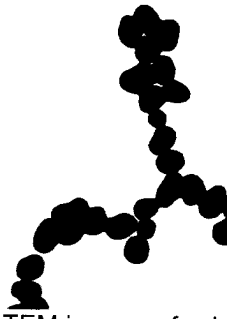
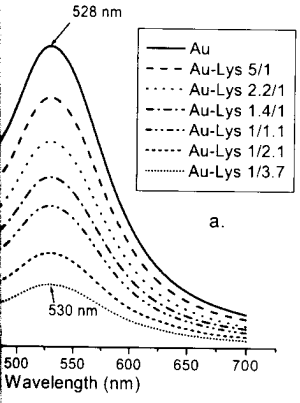
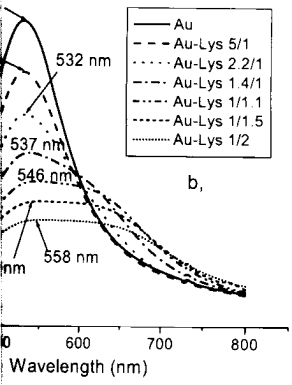


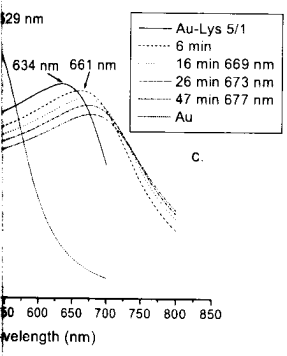
Fig.4. TEM images of gold
volume ratio 1:1 of aqueo

The atomic force m
multiple images, such as
mode operation. The asse

nent surrounding the gold
y the adsorbed layer.







ectrum of colloidal gold
0.01 M (a) and 0.1 M (b)
different ratios, and with
solution in time (c).

The color of the solution is changed from reddish to blue. This kind of color change is considered as an effect of the self-assembly or aggregation phenomenon [28, 29]. When the interparticle distance in the assemblies or aggregates decreases to less than about the average nanoparticle diameter, the electric dipole–dipole interaction and the coupling between the plasmons of neighboring particles result in the bathochromic shift of the absorption band.

Lysine adsorption on gold nanoparticles has been investigated [30], using 13 nm diameter gold particles and a $7 \cdot 10^{-4}$ M L-lysine solution at pH about 10.7. The UV-Vis spectrum showed a SPR peak at 520 nm, similar to that found for citrate coated nanoparticles. This result is similar to our results, using the most diluted lysine solution. By adding a condensing agent, the authors [30] observed that gold particles were aggregated by the formation of peptide bonds between two lysine molecules adsorbed on different gold nanoparticles. In the UV-Vis spectrum the SPR band of gold nanoparticles was shifted to 527 nm and a new broad peak appeared at 633 nm. For this situation, the spectrum is similar to that obtained by us at high concentrations of the lysine solution, pleading for assembly formation of gold nanoparticles mediated by lysine.

TEM images for gold nanoparticles with a 0.1 M lysine solution (Fig. 4) show both linearly ordered nanoparticles and more complex arrangements. Finally, these arrangements generate an almost ordered assembly of gold nanoparticles, mediated by lysine molecules, as also evidenced by AFM observations.

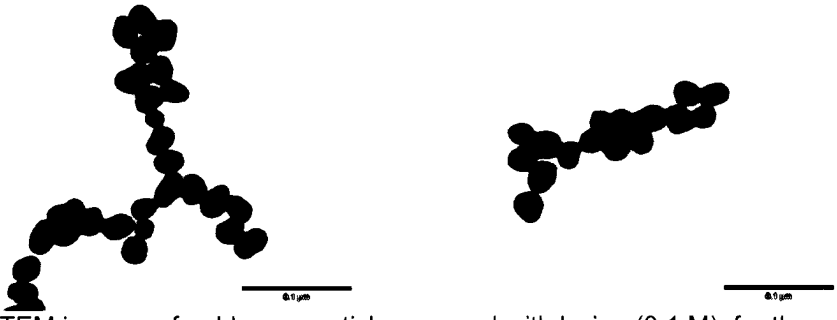


Fig.4. TEM images of gold nanoparticles capped with lysine (0.1 M), for the volume ratio 1:1 of aqueous solutions, at 30 sec after the mixing process.

The atomic force microscope allows simultaneous acquisition of multiple images, such as topography and phase images, under tapping mode operation. The assembly of gold nanoparticles, mediated by lysine,

was deposited on planar hydrophobic glass or on positively charged glass surfaces. Then, the assembly was observed by AFM under tapping mode and the structural features are visualized in Fig. 5. The two-dimensional topographic image (Fig. 5a) shows the morphology of an almost ordered

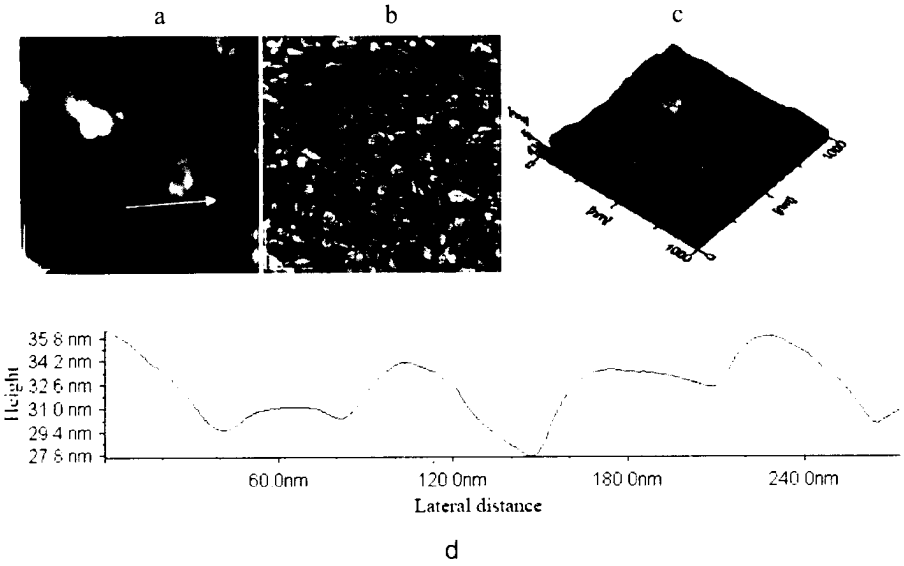


Fig. 5. 2D-topographic (a) and phase (b) AFM images of the assembly of gold nanoparticles, mediated by lysine, deposited on glass after one hour deposition time; scanned area 1000 x 1000 nm^2; 3D-view (c) of the topography (a); (d) cross section profile along the arrow in panel a; RMS of image panel (a) is 2.6 nm.

structure within domains, with small defects at domain boundaries. For this assembly of gold nanoparticles mediated by lysine, immobilized on planar glass surface, individual gold nanoparticles are visible from 2D-topography (Fig. 5a) and 3D-view (Fig. 5c). The image phase (Fig. 5b) show also that the assembly of gold nanoparticles mediated by lysine is almost compact.

The AFM images were acquired with high resolution as in the case of imaging assemblies of lipid molecules [22-26], assemblies of protein molecules [31, 32] or assemblies of gold nanoparticles mediated by different organic molecules [19], despite the structural complexity of molecules or of gold nanoparticles arrangements.

The AFM images evidence both the selectivity of lysine adsorption and its orientation on gold surface and the self-assembly process of gold nanoparticles within a compact network, as observed by UV-Vis spectroscopy (Fig. 3). Also, the gold nanoparticles appear almost ordered both in AFM images and in cross section profile (Fig. 5d) in substantial agreement with TEM images.

For lysine the bindir
achieved through the ε-amir
electrostatic interaction of th
the negatively charged citra
other hand, a direct bonding
be excluded (Fig. 6).

All the charged amir
gold surface, so are the amir
protonated), such as lysine
amino acid binding to gold
aggregates are schematized

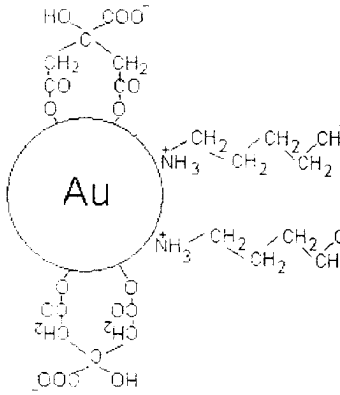


Fig. 6. Schema of lysine bind
formatio

Conclusions

Our investigations ind
be induced by lysine, an amir
i.e. ε-amine, besides the alph
and chemical properties of ar
basicity in various protolytic
substantial agreement with t
This effect could be explained
interactions between the cha
and bound to different gold na

The affinity of gold
development of new detect
diagnostics and biosensor
applications. On the other

was deposited on planar hydrophobic glass or on positively charged glass surfaces. Then, the assembly was observed by AFM under tapping mode and the structural features are visualized in Fig. 5. The two-dimensional topographic image (Fig. 5a) shows the morphology of an almost ordered

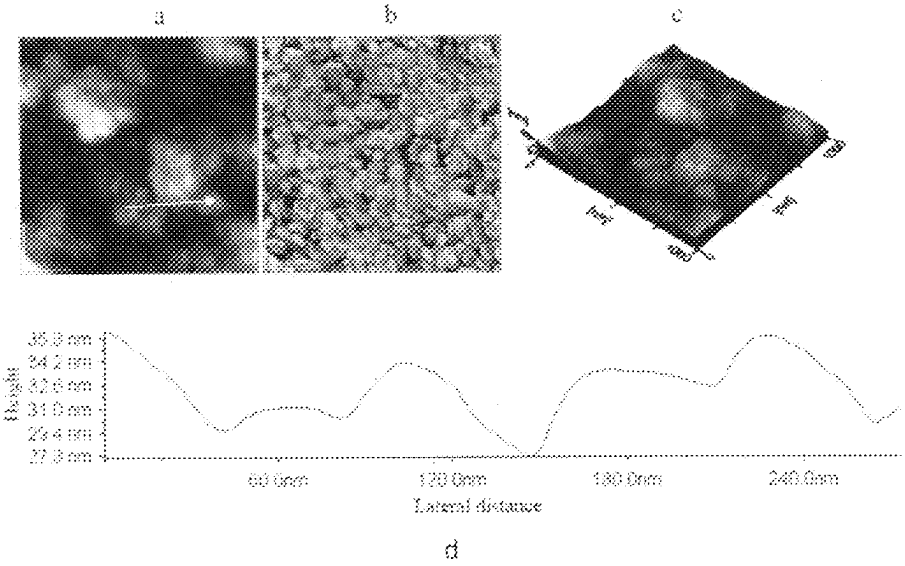


Fig. 5. 2D-topographic (a) and phase (b) AFM images of the assembly of gold nanoparticles, mediated by lysine, deposited on glass after one hour deposition time; scanned area 1000 x 1000 nm^2; 3D-view (c) of the topography (a); (d) cross section profile along the arrow in panel a; RMS of image panel (a) is 2.6 nm.

structure within domains, with small defects at domain boundaries. For this assembly of gold nanoparticles mediated by lysine, immobilized on planar glass surface, individual gold nanoparticles are visible from 2D-topography (Fig. 5a) and 3D-view (Fig. 5c). The image phase (Fig. 5b) show also that the assembly of gold nanoparticles mediated by lysine is almost compact.

The AFM images were acquired with high resolution as in the case of imaging assemblies of lipid molecules [22-26], assemblies of protein molecules [31, 32] or assemblies of gold nanoparticles mediated by different organic molecules [19], despite the structural complexity of molecules or of gold nanoparticles arrangements.

The AFM images evidence both the selectivity of lysine adsorption and its orientation on gold surface and the self-assembly process of gold nanoparticles within a compact network, as observed by UV-Vis spectroscopy (Fig. 3). Also, the gold nanoparticles appear almost ordered both in AFM images and in cross section profile (Fig. 5d) in substantial agreement with TEM images.

For lysine the bindi
achieved through the ε-ami
electrostatic interaction of th
the negatively charged citr
other hand, a direct bonding
be excluded (Fig. 6).

All the charged ami
gold surface, so are the ami
protonated), such as lysine
amino acid binding to gol
aggregates are schematized

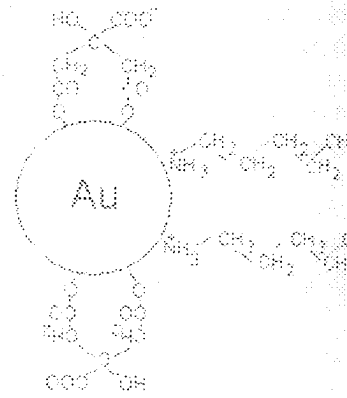


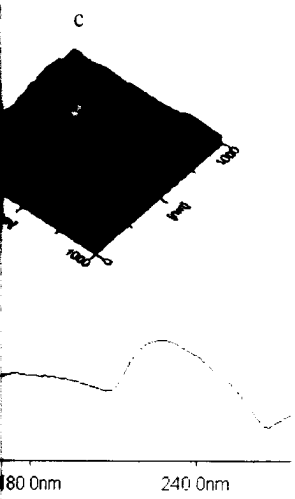
Fig. 6. Schema of lysine bind
formatio

Conclusions

Our investigations ind
be induced by lysine, an amir
i.e. ε-amine, besides the alph
and chemical properties of a
basicity in various protolytic
substantial agreement with t
This effect could be explained
interactions between the cha
and bound to different gold na

The affinity of gold
development of new detect
diagnostics and biosensor
applications. On the other

n positively charged glass
AFM under tapping mode
. 5. The two-dimensional
pgy of an almost ordered



s of the assembly of gold
after one hour deposition
e topography (a); (d) cross
age panel (a) is 2.6 nm.

main boundaries. For this
ne, immobilized on planar
sible from 2D-topography
e (Fig. 5b) show also that
sine is almost compact.
esolution as in the case of
mblies of protein molecules
liated by different organic
of molecules or of gold

ty of lysine adsorption and
ssembly process of gold
d by UV-Vis spectroscopy
rdered both in AFM images
eement with TEM images.

For lysine the binding with the gold nanoparticles surface may be achieved through the ε-amine group. The binding could occur through the electrostatic interaction of the lysine protonated ε-amine group ($-NH_3^+$) with the negatively charged citrate anions adsorbed on gold surface. On the other hand, a direct bonding of the amine group to the gold surface can not be excluded (Fig. 6).

All the charged amino acids present such strong interactions with gold surface, so are the amino acids that are usually *positively charged* (i.e. protonated), such as lysine (K), arginine (R) and histidine (H). A possible amino acid binding to gold nanoparticles and the formation of particle aggregates are schematized for lysine in Fig.6.

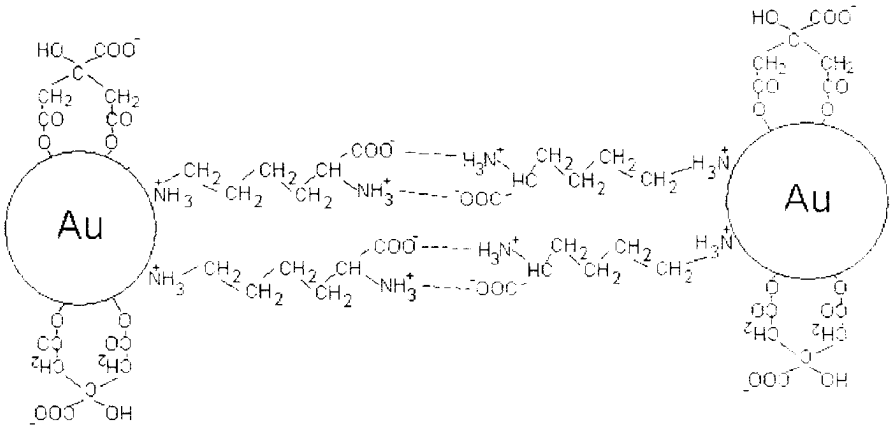


Fig. 6. Schema of lysine binding to citrate capped gold nanoparticles and bonds formation between gold nanoparticles.

Conclusions

Our investigations indicate that the assembly of gold nanoparticles can be induced by lysine, an amino acid possessing an additional functional group, i.e. ε-amine, besides the alpha-amine group. The correlation between physical and chemical properties of amino acids, such as hydrophobicity and acidity or basicity in various protolytic equilibria, and their molecular structure is in substantial agreement with their assembly effect on the gold nanoparticles. This effect could be explained primarily through the zwitterion-type electrostatic interactions between the charged amine and acid groups of lysine adsorbed and bound to different gold nanoparticles.

The affinity of gold nanoparticles towards lysine can lead to the development of new detection methods for analytical purposes, medical diagnostics and biosensors and to potential controlled drug delivery applications. On the other hand, the use of amino acids both in the

functionalization of gold nanoparticles and in the cross-linking of amino acid capped gold nanoparticles leading to stable self-assemblies are promising ways to the synthesis of nanostructured biomaterials. The stabilization of gold nanoparticles through amino acids is also important for the understanding of complex phenomena involved in the formation of new biomaterials by binding of proteins with gold nanoparticles with important implications in nanoscience and nanotechnology.

In future studies, the nanoengineering approach will be extended to explore the possible improvement in nanofabrication methods to reach amino acids and protein immobilization at molecular precision to control both the lateral and perpendicular orientations of functionalized gold nanoparticles. Definitely, the high-resolution engineering and imaging studies reveal the nanoscale and molecular level details for supramolecular chemistry and self-assembly processes, e.g., the influence of size, orientation and the local orders, with applications in bioscience [32]. Thus, the assemblies can be designed to contain the desired charged or chemical functionalities that will affect the intermolecular interactions such as van der Waals forces, hydrogen bonding, polar attractions and hydrophobic interactions.

Acknowledgement

This research was financially supported by the Romanian Ministry of Education and Research (Scientific research project no.5/2005, within the Excellency Research Program).

REFERENCES

1. M. Zheng, X. Huang, "Biofunctionalization of Gold Nanoparticles". In "Biofunctionalization of Nanomaterials", Editor: C.S.S.R. Kumar, Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, **2005**, pp. 99-124.
2. D. Fitzmaurice, S. Connolly, *Adv. Mater.*, **1999**, *11*, 1202-1205.
3. S. Mann, W. Shenton, M. Li, S. Connolly, D. Fitzmaurice, *Adv. Mater.*, **2000**, *12*, 147-150.
4. M. C. Daniel, D. Astruc, *Chem. Rev.*, **2004**, *104*, 293-346.
5. N. L. Rosi, C. A. Mirkin, *Chem. Rev.*, **2005**, *105*, 1547-1562.
6. J. C. Love, L. A. Estroff, J. K. Knebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.*, **2005**, *105*, 1103-1170.
7. G. M. Coppola, H. F. Schuster, "Asymmetric Synthesis. Construction of Chiral Molecules Using Amino Acids", Wiley, New York, 1987.
8. C. C. You, M. De, G. Han, V. M. Rotello, *J. Am. Chem. Soc.*, **2005**, *127*, 12873-12881.
9. R. Levy, R. C. Doty, "Sta
   the Peptide Route". In
   Kumar, Wiley-VCH Verla
10. J. Zsang, Q. Chi, J.U
    Langmuir, **2000**, *16*, 72
11. S. Mandal, S. Phadtare
12. P. R. Selvakannan,
    Langmuir, **2003**, *19*, 35
13. H. Joshi, P. S. Shiru
    Chem. B, **2004**, *108*, 1
14. Y. Shao, Y. Jin, S. Dor
15. S Mandal, P. Selva
    Proc.Indian Acad.Sc
16. P. Selvakannan, S.
    Adyanthaya, M. Sastry
17. S. Aryal, B.K. Remant,
    Sci., **2006**, *299*, 191-1
18. S.K. Bhargava, J.M. B
    32, 5949-5956.
19. O. Horovitz, A. Moca
    Boroştean, A. Popovi
    "Synthesis, Characteriz
    Aqueous Solutions in t
    Auto-Assembled Gold
    Micro-Nano-Biotechnol
    9, Editors: M. Zahares
    Romanian Academy Pr
20. M.J. Betts, R.B. Russ
    Substitutions". *In* "Bioi
    I.C. Gray, Wiley, **2003**
21. S. Chah, M.R. Hammo
22. M. Tomoaia-Cotisel, G
    Popa, *Studia, Univ. Ba*
23. M. Tomoaia-Cotisel, C
    Apetroaei, Gh. Popa, *S*
24. M. Tomoaia-Cotisel,
    Gh. Popa, *Rev. Roum*
25. M. Tomoaia-Cotisel,
    Apetroaei, Gh. Popa,
26. M. Tomoaia-Cotisel, V
    Ispas, O. Pascu, O. C
    50 (1), 23-37.
27. N.R. Jana, L. Gearhe
    922-927.
28. K.S. Mayya, V. Patil,
29. U. Kreibig, L. Genzel,

e cross-linking of amino acid
lf-assemblies are promising
rials. The stabilization of gold
tant for the understanding of
new biomaterials by binding
important implications in

pproach will be extended to
tion methods to reach amino
precision to control both the
onalized gold nanoparticles.
imaging studies reveal the
nolecular chemistry and self-
e, orientation and the local
us, the assemblies can be
mical functionalities that will
der Waals forces, hydrogen
tions.

by the Romanian Ministry of
roject no.5/2005, within the

n of Gold Nanoparticles". In
itor: C.S.S.R. Kumar, Wiley-
2005, pp. 99-124.
99, *11*, 1202-1205.
zmaurice, *Adv. Mater.*, **2000**, *12*,

104, 293-346.
105, 1547-1562.
luzzo, G. M. Whitesides, *Chem.*

ric Synthesis. Construction of
, New York, 1987.
l. Am. Chem. Soc., **2005**, *127*,

9. R. Levy, R. C. Doty, "Stabilization and Functionalization of Metallic Nanoparticles: the Peptide Route". In "Biofunctionalization of Nanomaterials", Editor: C.S.S.R. Kumar, Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, **2005**, pp. 235-269.
10. J. Zsang, Q. Chi, J.U. Nielsen, E.P. Friis, J.E.T. Andersen, J. Ulstrup, *Langmuir*, **2000**, *16*, 7229-7237.
11. S. Mandal, S. Phadtare, M. Sastry, *Curr. Appl. Phys.*, **2005**, *4*, 118-127.
12. P. R. Selvakannan, S. Mandal, S. Phadtare, R. Pasricha, M. Sastry, *Langmuir*, **2003**, *19*, 3545-3549.
13. H. Joshi, P. S. Shirude, V. Bansal, K. N. Ganesh, M. Sastry, *J. Phys. Chem. B*, **2004**, *108*, 11535-11540.
14. Y. Shao, Y. Jin, S. Dong, *Chem. Commun.*, **2004**, 1104-1105.
15. S Mandal, P. Selvakannan, S. Phadtare, R. Pasricha, M. Sastry, *Proc.Indian Acad.Sci. (Chem.Sci.)*, **2002**, *114*, 513-520.
16. P. Selvakannan, S. Mandal, S. Phadtare, A. Gole, R.Pasricha, S. D. Adyanthaya, M. Sastry, *J. Colloid Interface Sci.*, **2004**, *269*, 97-102.
17. S. Aryal, B.K. Remant, B. Narayan, C.K. Kim, H.Y. Kim, *J. Colloid Interface Sci.*, **2006**, *299*, 191-197.
18. S.K. Bhargava, J.M. Booth, S. Agrawal, P. Coloe, G. Kar, *Langmuir*, **2005**, *32*, 5949-5956.
19. O. Horovitz, A. Mocanu, Gh. Tomoaia, L. Olenic, Gh. Mihăilescu, O. Boroştean, A. Popoviciu, C. Crăciun, T. Yupsanis, M. Tomoaia-Cotişel, "Synthesis, Characterization and Properties of Gold Nanoparticles in Colloidal Aqueous Solutions in the Absence and in the Presence of Globular Proteins. Auto-Assembled Gold Nanostructures in Thin Films". In "Convergence of Micro-Nano-Biotechnologies", Series "Micro and Nanoengineering", **Volume 9**, Editors: M. Zaharescu, E. Burzo, L. Dumitru, I. Kleps and D. Dascalu, Romanian Academy Press, Bucharest, **2006**, pp. 132-146.
20. M.J. Betts, R.B. Russell, "Amino Acid Properties and Consequences of Substitutions". *In* "Bioinformatics for Geneticists", Editors: M.R. Barnes and I.C. Gray, Wiley, **2003.**
21. S. Chah, M.R. Hammond, R.N. Zare, *Chemistry & Biology*, **2005**, *12*, 323-328.
22. M. Tomoaia-Cotisel, Gh. Tomoaia, A. Mocanu, D.-V. Pop, N. Apetroaei, G. Popa, *Studia, Univ. Babes-Bolyai, Chem.*, **2004**, *49*(2), 167-181.
23. M. Tomoaia-Cotisel, Gh. Tomoaia, V.-D. Pop, A. Mocanu, O. Cozar, N. Apetroaei, Gh. Popa, *Studia, Univ. Babes-Bolyai, Phys.*, **2004**, *49* (3), 141-152.
24. M. Tomoaia-Cotisel, Gh. Tomoaia, V.-D. Pop, A. Mocanu, N. Apetroaei, Gh. Popa, *Rev. Roum. Chim.*, **2005**, *50*(5), 381-390.
25. M. Tomoaia-Cotisel, Gh. Tomoaia, V.-D. Pop, A. Mocanu, O. Cozar, N. Apetroaei, Gh. Popa, *Rev. Roum. Chim.*, **2005**, *50*(6), 471-478.
26. M. Tomoaia-Cotisel, V.-D. Pop, Gh. Tomoaia, A. Mocanu, Cs. Racz, C. R. Ispas, O. Pascu, O. C. Borostean, *Studia, Univ. Babes-Bolyai, Chem.*, **2005**, *50* (1), 23-37.
27. N.R. Jana, L. Gearheart, S.O. Obare, C.J. Murphy, *Langmuir*, **2002**, *18*, 922-927.
28. K.S. Mayya, V. Patil, M. Sastry, *Langmuir*, **1997**, *13*, 3944-3947.
29. U. Kreibig, L. Genzel, *Surface Sci.*, **1985**, *156*, 678-700.

30. L. Xu, Y. Guo, R. Xie, J. Zhuang, W. Yang, *Nanotechnology*, **2002**, *13*, 725-728.
31. M. Tomoaia-Cotisel, "The Nanostructure Formation of the Globular Seed Storage Protein on Different Solid Surfaces Studied by Atomic Force Microscopy", In "Convergence of Micro-Nano-Biotechnologies", Series "Micro and Nanoengineering", **Volume 9**, Editors: M. Zaharescu, E. Burzo, L. Dumitru, I. Kleps and D. Dascalu, Romanian Academy Press, **2006**, Bucharest, pp. 147 - 161.
32. G. Y. Liu, N. A. Amro, PNAS, **2002**, *99*, 5165-5170.

Preside

CARBON PASTE ELEC ZEOLITES AND MET DETECT

CODRUTA VARODI, D

ABSTRACT. Two new ele modified with Methyene Bl modified electrodes (MB- voltammetry and the ind surrounding solution was tested for electrocatalytic o an applied potential with n paste electrodes. The amp linear concentration range AA for MB-4A-CPEs. The regression equation and s MB-13X-CPEs and 1.7x10

Keywords: ascorbic acid paste electrode.

Introduction

L-Ascorbic acid (A compound playing a key formation of bone and conn helping burns and wounds h protecting cells against da products of normal cell acti widely used as a dietary s foods as an antioxidant f ascorbic acid content is very

Satisfactory techniq ideally be specific, reproduc electrochemical methods

* "Babes-Bolyai" University, Depa
Corresponding author: limur@ch