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Sub-nanomolar Detection of Biogenic Amines by SERS Effect Induced by Hairy Janus Silver Nanoparticles

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Abstract

Surface enhanced Raman scattering (SERS) is largely used as a transduction method for analytes detection in liquid and vapor phase. In particular, SERS effect was promoted by a plethora of different metal and semiconducting nanoparticles (NPs) and silver and gold nanoparticles appear particularly suitable for this application. Nevertheless, silver nanoparticles intrinsic propensity to aggregate in large clusters reduces the possibility to use naked nanoparticles in SERS applications, for this reason they are usually functionalized with organic molecules. This approach inhibits the aggregation process but, on the other hand, reduces the surficial area of the NPs able to interact with the analyte molecules. In the present work, we propose a simple method to obtain surficial anisotropic Janus silver nanoparticles: octadecylamine was used to stabilize the nanoparticles and to promote the deposition of the silver nanoparticles on a solid substrate. The AgNPs/octadecylamine nanostructures showed the typical "hairy" Janus morphology and a strong SERS effect was observed when two biogenic amines, i. e. 2-phenylethylamine and tyramine, were fluxed on the solid film. SERS phenomenon was studied as a function both of the chemical structure of the fluxed amine and of the distance between the aromatic moiety and the nanoparticle allowing to propose the AgNPs/octadecylamine Janus nanoparticles as an active layer for the detection of phenylethylamine and tyramine in picomolar concentration.

Keywords: Silver nanoparticles, Janus Nanoparticles, SERS, 2-phenylethylamine, tyramine

1. Introduction

Nanoparticles (NPs) with pronounced surficial anisotropy can exhibit unique and peculiar properties. With this goal, patchy [1] and Janus [2] nanoparticles have been synthesized and proposed for sensing and biosensing applications.[3] Janus particles are defined as NPs with two regions of their surface area covered by different chemical compounds that confer them strong anisotropic features.

A typical synthesis procedure for obtaining Janus nano- and micro-particles consists in a partial mask of the surface nanoparticles followed by a chemical or a physical functionalization.[2] In order to achieve the particles surficial modification, several techniques have been used such as, for example, the vapor deposition method[4], layer-by-layer technique[5], microfluidic approaches [6] and Pickering emulsion method.[7] Janus nanoparticles were also obtained dipping a substrate through an air/liquid interface [8-10] according with the Langmuir-Blodgett technique.[11] In the present work, by means of a simple modification of this method, floating films of hybrid organic/inorganic compounds were transferred on solid supports. The chemical affinity between an amphiphilic specie spread onto the aqueous interface, octadecylamine (ODA) and silver nanoparticles (AgNPs) suspended into the aqueous subphase was used to promote the formation of a chemical adduct (AgNPs/ODA).[12] The immobilization of the adduct on a solid support ensures the stabilization of AgNPs, inhibits their aggregation and guarantees a large area of nanoparticles' surface free from functionalization and potentially able to interact with other chemical species. In fact, the strong chemical affinity of silver nanostructures towards several molecules is well-known and they were used in different fields, such as biomedical,[13, 14] pharmacological[15, 16] and environmental applications.[17, 18] Furthermore, properly designed and developed silver nanoparticles have been used to promote SERS effect [19] towards an adsorbed molecule both as a consequence of plasmon resonance of the metal surface and as charge transfer.[20]

Moreover, it is worth reporting that the most used methods to obtain silver nanoparticles capped with organic substances are usually based on multi-step methods [21, 22] and the nanoparticle chemical physical properties are strongly dependent on many parameters that have to be monitored during the synthetic procedure [23, 24]. On the contrary, here a simple and rapid method is proposed allowing simultaneously to immobilize the AgNPs on solid supports and to improve their chemical stability promoted by a self-assembling mechanism formation of AgNPs/ODA adduct.

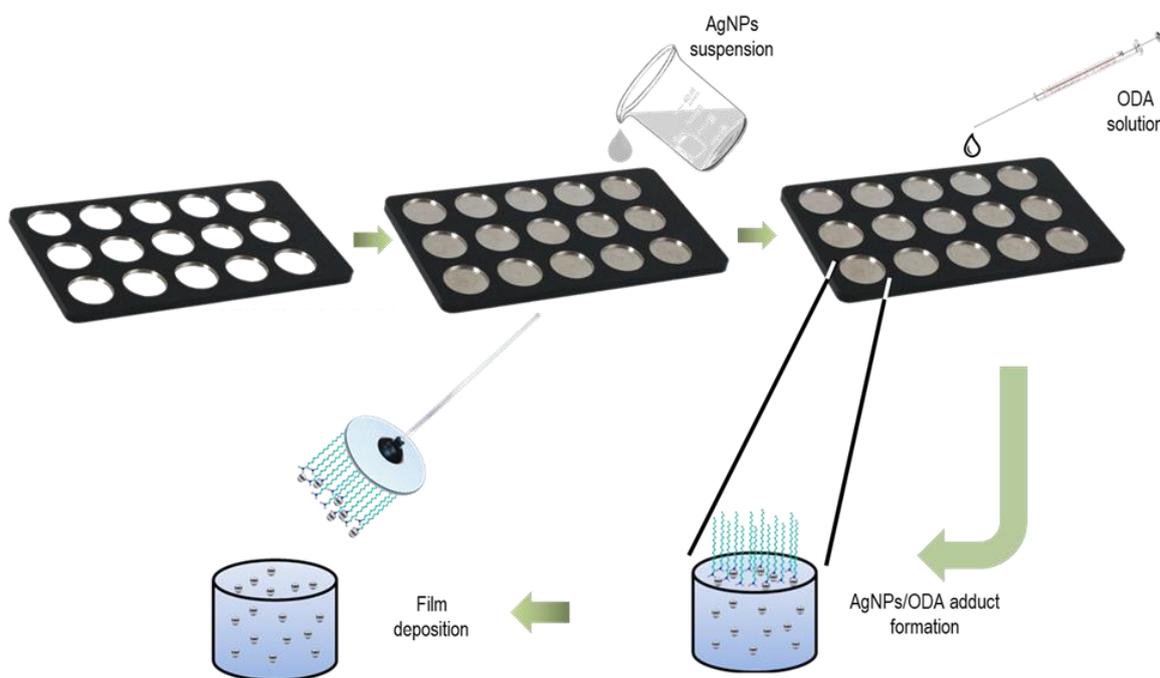
In this work, Janus silver nanoparticles were immobilized on a quartz substrate and non-resonant SERS mechanism towards phenyl amines was observed and studied, highlighting the possibility to specifically detect 10 pM of 2-phenylethylamine (PEA) and tyramine (TYR). These compounds are known as biogenic amines and they are produced in food and beverage as a consequence of fermentation and decomposition processes. [25] Many effects have been attributed to PEA and TYR, as for example headache, hypertension and food intolerances. [26] On the other side, these biogenic amines play an important role in the neurotransmission [27] and they are involved in many processes that interest the central nervous system. [28] For all these reasons, many efforts were produced in order to realize devices able to remove or detect small concentrations of PEA and TYR and more in general aromatic amines in liquid. [29-32] The peculiar physical transduction method (SERS phenomenon) used to reveal the analyte here proposed, ensured a highly selective sensing mechanism as well as a remarkable picomolar sensibility in the detection of PEA and TYR dissolved in aqueous solutions.

2. Materials and Methods

All the chemicals were purchased from Sigma Aldrich® and used without any further purification. Aqueous solutions were obtained using ultrapure water MilliQ grade.

A slight modification of the standard synthetic procedure reported in [33] was used to obtain silver nanoparticles. In particular, AgNO₃ 0.35 mM were dissolved in water in presence of NaBH₄ 0.8 mM. The solution was vigorously stirred at room temperature for 5 minutes until a yellowish solution was obtained. The colloidal Ag suspension was quickly transferred in a teflon multiwell and the ODA chloroform solution

(3.7 mM) was spread on the aqueous silver suspension. An aliquot of 2.8 μ L of ODA, corresponding to the maximum packaging of an ODA floating film on ultrapure water subphase (see supporting information file),^[34] was spread on each compartment of the teflon multiwell. The amphiphilic properties of the ODA induces the hydrophilic heads of the molecules ($-\text{NH}_2$ group) towards the aqueous/air interface and the hydrophobic tails far from the subphase.^[35] Further, amino groups interact with the silver nanoparticles suspended in the subphase allowing to form the AgNPs/ODA adduct directly at the interface. Grazing on the air/subphase interface with a solid hydrophobized substrate the floating film of silver nanoparticles and ODA was deposited on the solid support. [32, 35] In the Scheme 1, a schematization of the film formation and transfer on solid substrate is reported.



Scheme 1. Sketch of the method used to transfer the AgNPs/ODA adduct from the liquid/air interface onto a solid support

Raman spectroscopy was carried out by a NRS-4500 JASCO Confocal Raman equipped with a 532 nm laser source (power 1.5 mW). Each sample was scanned by 50 accumulations and repeated on 5 different points and then an average of Raman intensities was graphed. UV-Visible spectra in the range 300 nm – 800 nm was recorded by a Shimadzu UV-2600 Spectrophotometer.

Transmission electron microscopy (TEM) was carried out by a JEOL JEM 1400 microscope operated at an accelerating voltage of 80 kV with a Lanthanum hexaboride (LaB6) source. More in detail, AgNPs samples for TEM analysis were prepared by sonicating the particles suspensions in an ultrasonic bath for 20 min in water. A drop of the dispersion was then placed onto carbon-supported copper grids and dried at room temperature and then in stove at 50°C allowing the complete elimination of water. The AgNPs/ODA adduct was directly transferred on TEM grids according with the procedure reported below. Samples were dried as previously described.

3. Results and discussion

3.1 AgNPs/ODA adduct formation and transfer process on solid substrates

UV-visible spectroscopy was carried out both on the AgNPs suspension and on the film transferred on a quartz slide (deposition procedure was repeated two times on the substrate) in order to study the spectral profile of the silver plasmon peak and to confirm the transfer of the AgNPs/ODA adduct (Figure 1).

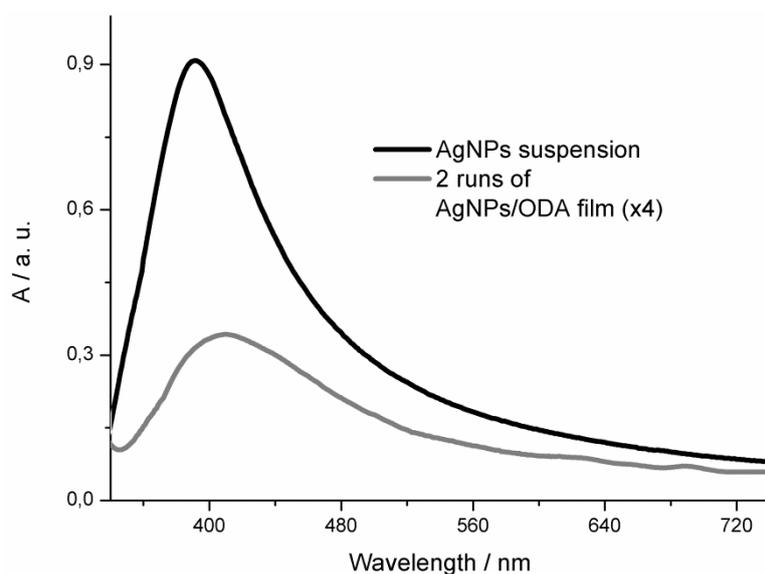


Figure 1. Visible spectra of AgNPs suspension (black line) and solid film of AgNPs/ODA (grey line) obtained repeating two times the deposition procedure (2 runs). Spectrum of AgNPs/ODA film was 4 times magnified for clarity.

Plasmon peak of AgNPs suspension is located at 395 nm and it suggests that polydisperse spherical nanoparticles are formed during the synthesis. [36] Besides the peak centered at 395 nm, a strong signal at 410 nm appears on the solid film and it can be attributed to the dipole–dipole couplings of nanoparticles clustered during the deposition process. [37] The visible spectroscopy confirms that the AgNPs/ODA adduct is obtained at the air/liquid interface and transferred on the solid support.

Both Ag nanoparticles and AgNPs/ODA adduct were characterized by transmission electron microscopy. Confirming the observation pointed out by visible spectroscopy, silver nanoparticles appear spherically shaped with a diameter comprised from about 10 nm up to 50 nm (Figure 2a) and large naked nanoparticles aggregates can be observed as a consequence of the well-known aggregation phenomena among the silver nanoparticles.[38]. More interesting is the morphology of the AgNPs transferred on the solid substrate by means of the ODA. A uniform distribution of the nanoparticles dimension (with a diameter of about 40 nm) was observed for the Ag/ODA NPs if compared with the as-synthesized silver nanoparticles (Figure 2b). Furthermore, a clear-cut asymmetry on the nanoparticles surface can be observed (Figures 2c, 2d and 2e): a thick crown is present on the nanoparticles suggesting that the nanoparticles-octadecylamine adduct is formed at air/liquid interface and transferred on the solid substrate. So, TEM images suggest that the interaction between the water suspended nanoparticles and the ODA floating film takes place only on the surface of the AgNPs at the air/liquid interface promoting the formation of the so-called hairy Janus nanoparticles.[39] The length of the organic moiety present on the decorated silver nanoparticles suggest that a floating layer of ODA thicker than a monolayer is formed at the subphase/air interface.

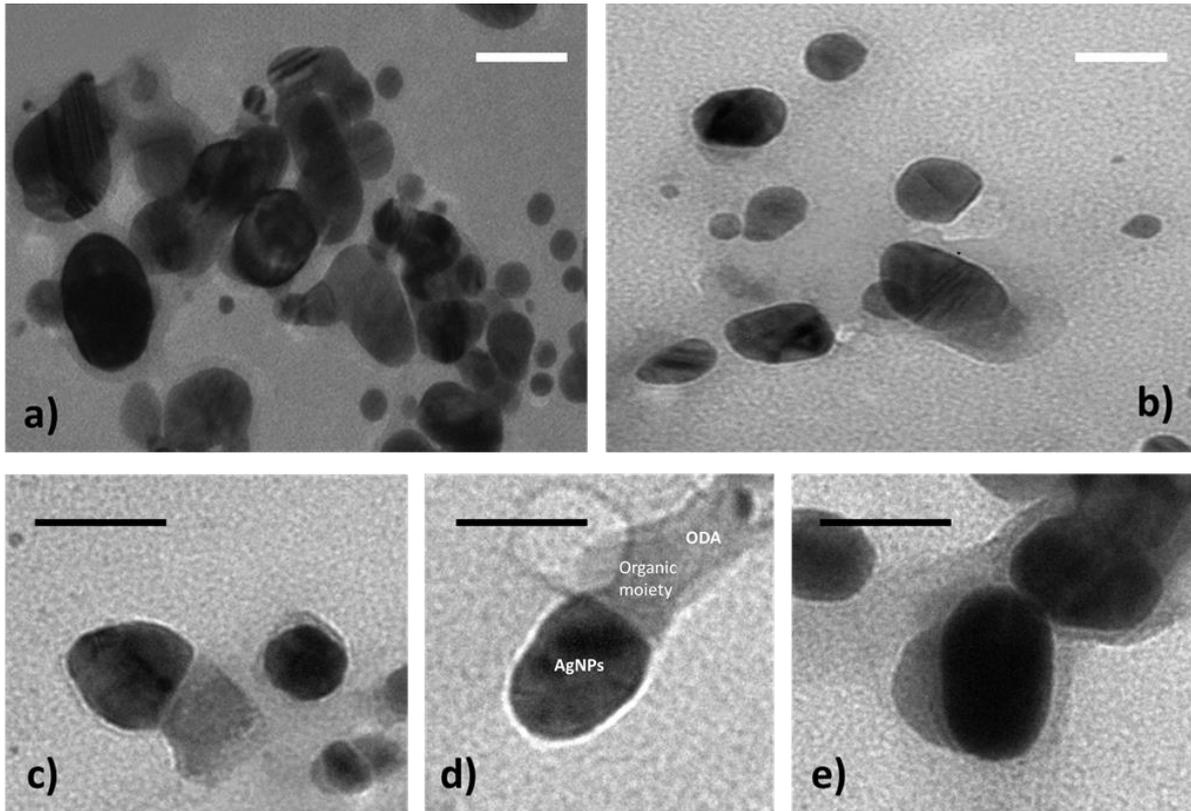


Figure 2. TEM pictures of a) naked silver nanoparticles of different dimensions and of b) Ag/ODA nanostructures. c), d) and e) highlight the anisotropic features of the Ag/ODA adduct transferred directly on the TEM grids (scale bar: 50 nm). In the box d, inorganic and organic moieties of AgNPs/ODA adduct were labeled

Raman spectra of the AgNPs/ODA adduct confirmed the interaction between the amino group of ODA and the inorganic nanoparticles (Figure 3). In fact, the sharp and intense signal at 235 cm^{-1} in the spectrum of the adduct clearly suggests the formation of a chemical bond between AgNPs and the $-\text{NH}_2$ group of ODA. [40] It is interesting to observe that in conjunction with the signal imputable to the Ag- NH_2 interaction, the Raman band related to the $-\text{NH}_2$ stretching vibration at 3075 cm^{-1} present in the ODA spectrum disappears when the adduct is formed (inset in Figure 3). This observation further confirms that the amino group is mainly involved in the interaction with silver nanoparticles. The other signals of ODA are present almost unchanged in both the spectra.

Raman spectroscopy was also used to investigate the interaction between the “naked face” of the silver nanoparticles and different amines dissolved in water. In particular, aliphatic amine 2-aminoheptane aqueous solution (10^{-3} M) was fluxed on AgNPs/ODA film and the Raman spectrum was recorded (Figure 3). Signals imputable to antisymmetric deformations and bending modes of $-CH_2$ group can be observed between 1445 and 1486 cm^{-1} and in the range $1190 - 1030\text{ cm}^{-1}$ respectively,[41] and they appear more intense than those ones observed in the AgNPs/ODA spectrum, suggesting that the interaction between Janus nanoparticles and aliphatic amines take places. Furthermore, the absence of $-NH_2$ stretching vibration modes of 2-aminoheptano, as well as observed in the AgNPs/ODA spectrum, suggests that the interaction between the aliphatic amine dissolved in water and the AgNPs/ODA adduct mainly involves the amino group of 2-aminoheptano that chelates the naked face of silver nanoparticles.

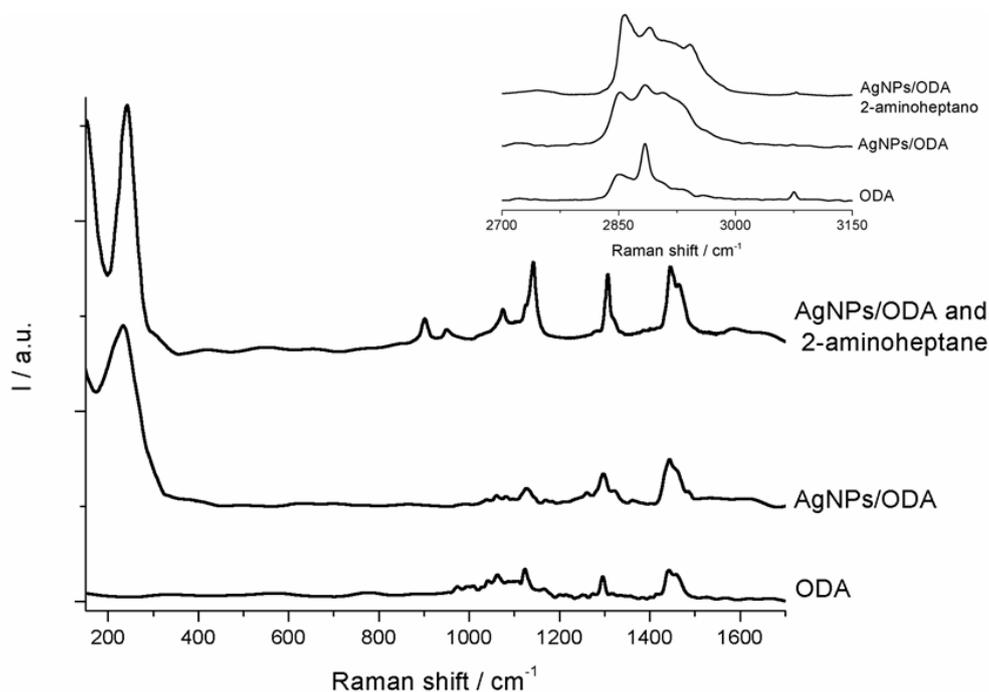


Figure 3. Raman spectra of ODA, AgNPs/ODA and AgNPs/ODA after the interaction with 10^{-3} M aqueous solution of 2-aminoheptane

3.2 SERS mechanism promoted by the AgNPs/ODA adduct

Raman spectra obtained when 2-phenethylamine (PEA) aqueous solution are fluxed on the AgNPs/ODA thin film are reported in Figure 4 (in figure S1 the Raman spectrum of PEA cast film is reported). PEA is a biogenic amine [29] abundant in chocolate,[42] wine,[43] cheese [44] and it can be chemically substituted in order to obtain amphetamine and drugs acting as stimulants and antidepressant. Furthermore, more recently, its important role in many processes that involve central nervous system has been pointed out. [45]

PEA aqueous solution (10^{-3} M) was fluxed on the AgNPs/ODA solid film and the signals imputable to the aromatic moiety of PEA appeared very intense. A comparison between PEA cast film (10^{-3} M) and 10^{-3} M of PEA fluxed on AgNPs/ODA film clearly shows that a strong enhancement of biogenic amine signals is obtained (Figure S2). The sharp and intense signals at 1003 and 1020 cm^{-1} can be attributed at the benzene breathing of PEA as well as the bands in the region 1200 cm^{-1} and 1600 cm^{-1} are imputable to the ring asymmetric deformations [21, 46]. The interaction between the fluxed PEA and the active adduct is detectable by Raman spectroscopy up to 10 picomolar concentration of the PEA. It is evident that an enhancement of the amine signals is promoted by the presence of the AgNPs/ ODA adduct. Although the exact distinction of resonant from non-resonant enhanced Raman spectroscopy is often complex [47], some evidences suggest that in the present case both the charge transfer mechanism and electromagnetic coupling phenomenon rule Raman PEA signal amplification [48]. In fact, even though the absorption spectrum of AgNPs/ODA film is centered at 395 nm, its broad SPR peak can couple with the Raman laser source at 532 nm promoting a surface enhancement of the Raman modes [48]. On the other side, an evidence of the enhancement of PEA Raman signals ruled by charge-transfer mechanism is suggested by the stronger amplification of the asymmetric vibration modes of PEA if compared with their benzene symmetric modes, about 50 times and 10 times respectively (Figure S2) [46, 47, 49-52]. The chemical bond between analyte and metal surface increases the effective volume of the molecule, increasing the ground state polarizability resulting in a charge transfer from molecule to metal surface [51].

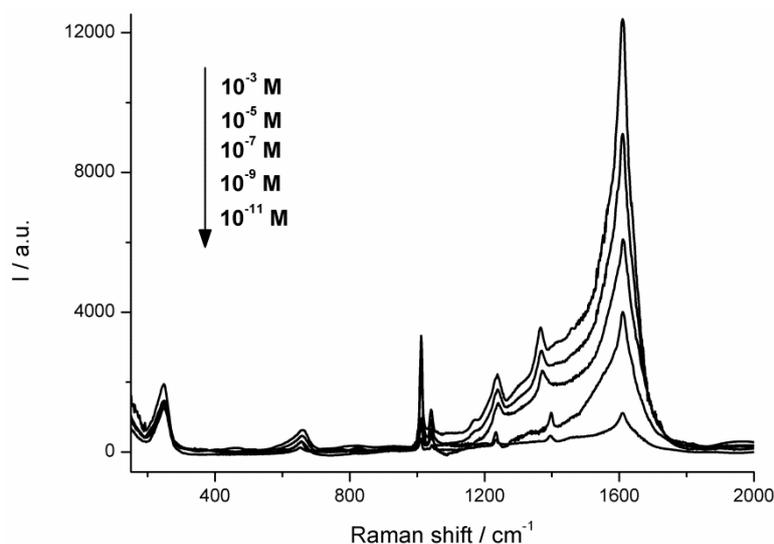
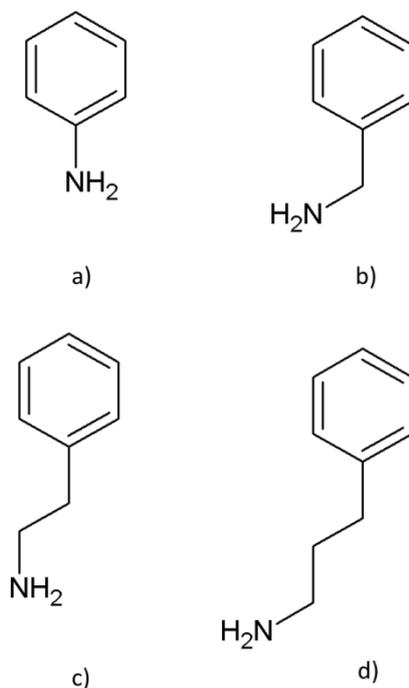


Figure 4. Raman spectra of PEA enhanced by the coupling with AgNPs/ODA.

In order to further confirm that the SERS mechanism is ruled by the charge transfer, the influence of the aliphatic chain length on the enhancement phenomenon was evaluated. Same procedure was repeated fluxing aniline, benzylamine and 3-phenyl-1-propylamine (Scheme 2) aqueous solutions. Even though the SERS mechanism of aniline in presence of silver nanoparticles is one of the most reported example of application of surface enhanced Raman spectroscopy,[53, 54] AgNPs/ODA did not promote any enhancement of the signals neither of aniline nor of benzylamine (Figures S3, S4 and S5). It could be a consequence of the reduced distance between the aromatic moiety of the amines and silver-based adduct that induces a more rapid relaxation from the excited state reducing the enhancement of the SERS effect. With this aim, a carbon atom was added to the aliphatic chain of PEA and the interaction between AgNPs/ODA and 3-phenyl-1-propylamine was investigated by means of Raman spectroscopy. An enhancement of the Raman signals of the water dissolved amine was recorded (Figure S5), even though the phenomenon appears drastically reduced if it is compared with the SERS effect observed on the PEA Raman bands. As well as PEA, the Raman bands ascribable to the aromatic moiety of 3-phenyl-1-propylamine are enhanced by the non-resonant SERS, but the longer aliphatic chain reduces the sensitivity of the transduction method. This experimental evidence seems to confirm what already discussed in the case of

PEA signals enhancement, that is both resonant and charge transfer mechanisms are responsible of the observed SERS phenomenon.



Scheme 2. Chemical structures of the amines used to evaluate the influence of the distance between the amino group and the aromatic ring: a) aniline, b) benzylamine, c) PEA and d) 3-phenyl-1-propylamine.

3.3 Biogenic amines detection

An interesting observation about the sensing properties of AgNPs/ODA towards PEA molecules is the logarithmic dependence of the peak at 1610 cm^{-1} on the analyte concentration (Figure 5a). Linear fit of the Raman intensity at 1610 cm^{-1} as a function of the natural logarithm of PEA concentration suggests that the proposed system could be used as a highly sensible (by means of the enhancement induced by the chemical physical mechanism used as transduction method) and a highly selective (the SERS mechanism takes place only under peculiar conditions) sensor for PEA detection in aqueous solution.[55]

The detection of tyramine, another biogenic amine with a chemical structure similar enough to that one of PEA (Figure S6), was evaluated by means of the charge transfer SERS phenomenon. In Figure 5b, the Raman spectra of AgNPs/ODA when aqueous solutions of TYR at different concentrations were fluxed are

reported. As observed in the case of PEA, an enhancement of the aromatic bands of the biogenic amine was observed. In fact, the signal at 1590 cm^{-1} imputable to the aromatic ring vibrations [56] appears very intense and detectable up to a concentration of 10^{-11} M ; furthermore this band is stronger than the HNH group bending, usually the most intense peak in the range $200\text{ cm}^{-1} - 2000\text{ cm}^{-1}$ in the TYR Raman spectrum.[56] As observed for PEA, the intensity of the Raman signal of TYR aromatic ring vibration dependence on the analyte concentration is ruled by a logarithm trend (inset in Figure 5b).

Finally histamine, another well-known biogenic amine (Figure S7), was fluxed on the solid film of AgNPs/ODA adduct. In this case, SERS phenomenon between the nanoadduct and the biogenic amine appears inhibited (Figure S8). A possible rationale can be proposed considering that the aromatic moiety of histamine is represented by an imidazole group that can interact with the Ag nanoparticles (Figure S9). This chemical interaction reduces the distance between molecule and the adduct, affecting the SERS mechanism confirming the high selectivity of the transduction method for PEA and TYR detection.

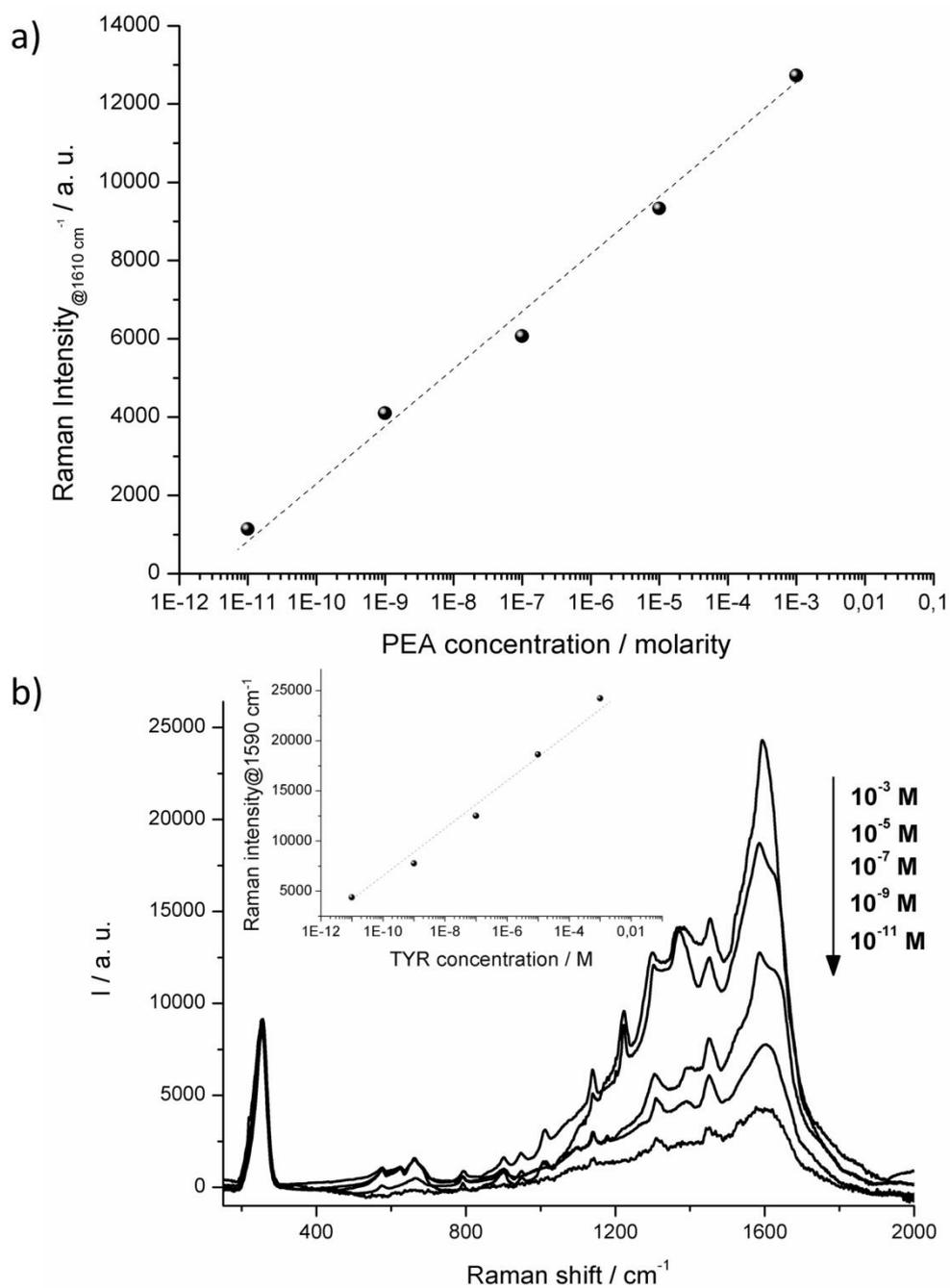


Figure 5. a) Logarithmic dependence of Raman intensity of the aromatic ring deformations band on PEA concentration. b) SERS spectra of TYR obtained by fluxing different analyte concentrations and dependence of Raman intensity of the band at 1590 cm⁻¹ and TYR concentration (inset in box b).

4. Conclusions

Janus silver nanoparticles were obtained by means of a simple procedure, i.e. the amphiphilic properties of aliphatic octadecylamine molecules were used to anchor the water suspended naked silver nanoparticles.

Silver nanoparticles with the surface partially covered by octadecylamine and partially uncovered were transferred on a solid support simply grazing the interface with a solid substrate. The transferred adduct was characterized by UV-visible spectroscopy and the TEM images showed the typical “hairy” Janus nanoparticles. Non-resonant SERS was observed when two biogenic amines, 2-phenylethylamine and tyramine, were fluxed in aqueous solution on the solid active layer, allowing to detect them up to 10^{-11} M concentration. The SERS phenomenon was studied as a function of the distance between the amino group and the aromatic moiety of the fluxed amine evidencing the crucial role played by the distance in the charge transfer process and conferring high selectivity to the sensing mechanism.

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