Magneto-Plasmonic Colloidal Nanoparticles Obtained by Laser Ablation of Nickel and Silver Targets in Water

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ABSTRACT: Stable magneto-plasmonic nanoparticles in colloidal suspensions are fabricated by two-step nanosecond-pulsed laser ablation of nickel and silver targets in pure water and characterized by UV–visible absorption, Raman, X-ray photoelectron spectroscopic, and magnetic measurements, along with high-resolution electron microscopy analysis. These systems are constituted by a low-crystallinity matrix of ferromagnetic nickel hydroxide, where nickel oxide nanocrystals are embedded, with silver nanoparticles intimately linked to them. The surface enhanced Raman scattering activity is assessed by adsorption of adenine as probe ligand. Spectroscopic investigation and density functional theory calculations revealed that adenine is linked to nickel oxide, while nanosilver essentially plays the role of ensuring the Raman enhancement for the adsorbed organic ligand. Both magnetic and plasmonic properties allow using these nanostructured bimetallic platforms as catalysts in chemical reactions or nanosensors in biomedicine as well as in environmental research.

INTRODUCTION

Due to the nature of transition metals, nanosized nickel has found applications in the fields of magnetic devices,1,2 catalysts,3 batteries,4 fuel cells,5,6 and solar cells,7 among others. Hence, the synthesis of Ni nanoparticles has attracted considerable attention. The PLAL (pulsed laser ablation in liquid) technique allows obtaining Ni nanoparticles without reactants and byproducts in colloidal suspensions.9,10 However, when water is used as solvent, oxidized nickel nanoparticles are expected, due to the presence of oxygen dissolved in the aqueous environment. This can be a quite important result, because nanosized NiO is increasingly utilized in various fields as an efficient catalyst in the processes of decomposition, synthesis, and transformation of organics, and as a gas sensor in environmental investigation or biosensor in biomedical applications.11−18 In the bulk, whereas Ni is ferromagnetic, pure NiO exhibits insulating character and antiferromagnetic ordering at room temperature.19 Reducing the material size to the nanoscale, however, the resulting magnetic properties of NiO nanoparticles can be very complex depending on finite size effects and surface effects.20 In the present report, we have obtained magnetic nanoparticles by nanosecond-pulsed laser ablation of nickel in water and characterized them by spectroscopic and microscopic techniques. In addition, bimetallic (Ni−Ag) colloidal nanoparticles have been fabricated by successive ablation of silver in order to combine magnetic and catalytic properties, due to the nickel-containing nanoparticles, with the SERS (surface-enhanced Raman scattering) activity,21 ensured by the presence of nanosized silver. In the SERS effect, the strong localization of the electromagnetic field associated with the collective excitation waves, usually called plasmons, of the electrons localized at the nanostructured surface of metals with high optical reflectivity, such as silver, gold, and copper, allows obtaining enhancements of several orders of magnitude (usually up to 107 factors) for the Raman response of the adsorbed molecules. In addition to this mechanism, also a chemical enhancement contribution, which usually provides Raman enhancement factors up to 103, can be
effective, due to the perturbation of the molecular polarizability because of the formation of chemical complexes of the molecules with the active sites of the metallic surface. Hence, SERS spectroscopy allows identifying, at trace level, reactants, products, or byproducts of reactions occurring where they take place, on the surface of the metal nanoparticles. Here we have employed a two-step laser ablation to fabricate nanosized bimetallic systems, made of nickel, with a strong performance in heterogeneous catalysis, and silver, as SERS-active metal. This preparation consists in performing the laser ablation of a nickel target in pure water, followed by a successive laser ablation of a silver target in the same colloidal dispersion resulting from the first ablation.

The aim of the present investigation is obtaining Ni–Ag nanocomposites to be employed as both catalysts and nanosensors, exploiting also their magnetic response, which could be useful in biomedicine and in environmental research, due to the particle mobility under a magnetic field, allowing the transport of drugs in body fluids or the removal of contaminants in waters. Bimetallic nanosystems are usually prepared by following chemical routes, with consequent issues due to the presence of surfactants, organic stabilizers, reducing agents, and reduction byproducts, which could cause interference in the SERS measurements, impairing the detection of the title analytes. The present work, based on the laser ablation of a nickel target, and successively of a silver target, in pure water in order to bypass the above purity problems, is, to our knowledge, the first work on nanoparticles containing nickel and silver obtained by this technique. The structural, spectroscopic, magnetic, and plasmonic characterization of our bimetallic nanocomposites has been performed by UV–vis absorption, XPS (X-ray photoelectron spectroscopy), Raman spectroscopy, and TEM (transmission electron microscopy)/STEM (scanning/transmission electron microscopy), along with magnetization measurements at different temperatures. In particular, the SERS response has been tested by adopting adenine as probe molecule and analyzing the Raman data with the DFT (density functional theory) by adopting adenine as probe molecule and analyzing the Raman data with the DFT (density functional theory) computational approach. This latter, based on model systems constituted by ligand molecules bound to adatoms or adclusters with one or few metal atoms, cannot reproduce the electromagnetic SERS enhancement, but it is generally sufficient to simulate the SERS profiles of the chemisorbed species, including band positions and relative intensities. In addition, these DFT calculations can provide information on the type of adsorbed species and of metal active sites, as well as on the molecular sites of interaction with the substrate.

### EXPERIMENTAL SECTION

**Materials.** Nickel (0.25 mm thickness, 99.9% purity) and silver (0.5 mm thickness, 99.9% purity) targets were purchased from Aldrich. Colloidal suspensions were prepared by laser ablation in deionized water (18.2 MΩ cm at 25 °C) and characterized within 2 h from the preparation.

**Laser Ablation.** Laser ablation of nickel and silver targets was performed with the fundamental wavelength (1064 nm) of a Q-switched Nd:YAG laser (Quanta System G90-10; repetition rate 10 Hz, pulse width 10 ns). We performed the laser ablation of a nickel target in pure water, in order to obtain the Ni colloid; a part of this latter was used as aqueous medium for the successive laser ablation of silver target, in order to obtain the bimetallic Ni–Ag colloid. The laser pulse energy was set at 20 mJ/pulse (200 mW) with a laser spot of approximately 1 mm diameter and corresponding fluence of 2.5 J/cm². The target plate was fixed at the bottom of a glass vessel filled with ~6 mL of liquid (height above the target 2 cm). The irradiation time of the metal targets was about 20 min. To minimize effects due to crater formation in the metal target, the glass vessel was manually rotated and translated, stopping the ablation process every 3'. The laser pulse entered the vessel from above, thus impinging perpendicularly onto the target.

**Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) Measurements.** The determination of the Ni/Ag concentration ratio in the bimetallic colloidal suspension was performed in triplicate by a Varian 720-ES inductively coupled plasma atomic emission spectrometer (ICP-AES).

**C Potential Measurements.** C-Potential and dynamic light scattering (DLS) analysis were performed with a Zetasizer Nano ZS90, Malvern Instruments. The temperature was fixed at 25 °C. Particle size measurements, obtained by dynamic light scattering, range from 0.3 nm (diameter) to 5 μm, using 90° scattering optics.

**UV–Visible Absorption Measurements.** UV–vis absorption spectra of colloid suspensions were obtained in the 200–800 nm region by using a Cary 5 Varian spectrophotometer.

**XPS Measurements.** XPS measurements were performed in an ultrahigh vacuum (UHV; 10⁻⁹ mbar) system equipped with a VSW HAC 5000 hemispherical energy analyzer and a nonmonochromatized Mg Kα X-ray source (1253.6 eV).

**Visible Absorption Measurements.** UV–vis absorption spectra of colloidal suspensions were obtained in the 200–1000 nm spectral range.

**XPS Measurements.** XPS measurements were performed in an ultrahigh vacuum (UHV; 10⁻⁹ mbar) system equipped with a VSW HAC 5000 hemispherical energy analyzer and a nonmonochromatized Mg Kα X-ray source (1253.6 eV). The sample power was 120 W (12 kV × 10 mA) and the spectra were acquired in the constant-pass-energy mode at Eps = 22 eV. The overall energy resolution was 1.2 eV as a full width at half-maximum (fwhm) for the Ag 3d⁵/₂ line of a pure silver reference. The recorded spectra were fitted using CasaXPS software employing Gauss–Lorentz curves after subtraction of a Shirley-type background. The sample was introduced in the UHV system via a loadlock under inert gas (N₂) flux, in order to minimize the exposure to air contaminants and kept in the introduction chamber for at least 12 h before the measurements.

**Raman Measurements.** Micro-Raman spectra of metal nanoparticles deposited on an aluminum plate were measured by a Renishaw RM2000 instrument, equipped with a diode laser emitting at 785 nm. Sample irradiation was accomplished by using the 50X microscope objective of a Leica Microscope DMLM. The backscattered Raman signal was fed into the monochromator through 40 μm slits and detected by an air-cooled CCD (2.5 cm⁻¹ per pixel) filtered by a double holographic Notch filters system. Spectra were calibrated with respect to a silicon wafer at 520 cm⁻¹.

SERS spectra in the Ni–Ag colloid were measured after addition of adenine (Aldrich, purity ≥99%) in 2.5 × 10⁻⁵ M concentration, by using the 514.5 nm line of a Coherent argon ion laser, a Jobin-Yvon HG2S monochromator equipped with a cooled RCA-C31034A photomultiplier, and a data acquisition facility. To reduce the thermal effects due to the laser light, a defocused beam with low power (50 mW) was used for irradiating the colloidal samples. Power density measurements were performed with a power meter instrument (Model 362; Scientech, Boulder, CO, USA) giving ~5% accuracy in the 300–1000 nm spectral range.

**Electron Microscopy Analysis.** To prepare the specimen for TEM (transmission electron microscopy) and STEM (scanning/transmission electron microscopy) analysis, the samples were dispersed in ethanol by ultrasonication and a
drop of this dispersion was placed on a holey carbon grid and dried. TEM/STEM analysis at both 80 and 200 kV was performed on an FEI Titan ChemiSTEM equipped with probe corrector, Super-X EDS detector, and Gatan EELS spectrometer. EDS (energy dispersive X-ray spectrometry) quantification was carried out by employing the Cliff–Lorimer method in Esprit Software.

**Magnetic Measurements.** Magnetic measurements were performed on dry powder samples by a superconducting quantum interference device (SQUID) magnetometer (MPMS-XL7 Quantum Design Ltd.) as a function of the magnetic field (up to ±50 kOe) at different temperatures in the interval 2–300 K. Magnetization induced by a 1 kOe static magnetic field was recorded as a function of temperature (5–300 K). Samples were always cooled down in the absence of a magnetic field.

**Computational Details.** Density functional theory (DFT) calculations for model systems constituted by adenine linked to Ag⁺ ion or to a NiO molecule were carried out using the Gaussian 09 package, along with the B3LYP hybrid exchange and correlation functional, along with the LanL2DZ combined pseudopotential and basis set. The latter has been chosen because it provides good structural and spectroscopic properties in metal-hybrid nanoclusters in a reasonable computational time.32,33

The molecular structures of the adenine complexes with silver or nickel oxide and the corresponding vibrational frequencies were computed adopting tight convergence criteria. By allowing all the parameters to relax, the optimized geometries corresponded to true energy minima, as revealed by the lack of imaginary values in the vibrational mode calculations.

The calculated Raman activities (A_i) were converted to relative Raman intensities (I_i) using the following relationship, as reported in the literature:34,35

\[ I_i = f(I_0 - v_i)^4 A_i/I_0[1 - \exp(-h\nu_i/kT)] \]

where \(\nu_0\) is the exciting frequency (in cm\(^{-1}\) units), \(v_i\) is the vibrational frequency (in cm\(^{-1}\) units) of the \(i\)th normal mode, \(h\), \(c\), and \(k\) are fundamental constants, and \(f\) is a suitably chosen common normalization factor for all peak intensities.

### RESULTS

**Colloidal Stability.** The preparation protocol of the colloid obtained by ablation of the Ni target, hereafter called Ni colloid, and of that obtained by two-step ablation of Ni and Ag targets, hereafter called Ni–Ag colloid, is shown in Figure 1A. Both colloids are quite stable, as evidenced by strong positive ζ-potential values, +34.2 and +28.0 mV for the Ni and Ni–Ag colloids, respectively. The positive ζ-potential values suggest that nickel is oxidized. In this case the oxygen atoms, which have negative partial charges and are exposed to the aqueous solvent, are able to attract positively charged species (for example, hydroxonium cations, H\(_3\)O\(^+\)), determining positive ζ-potentials. For Ag nanoparticles, instead, the metal surface exposed to the aqueous solvent assumes a positive partial charge, allowing the adsorption of hydroxide anions and determining negative values of the ζ-potential, as reported in the literature. This explains why the laser ablation of silver in the colloid obtained by nickel ablation provokes a decrease of the (positive) ζ-potential.

The Ni/Ag weight ratio of the Ni–Ag colloid, as determined by ICP-AES measurements, is 1.59; by increasing the silver content produced by laser ablation, the value of ζ-potential further decreases, with consequent colloidal instability.

Figure 1B shows the effect of magnetic attraction due to a magnetic stir bar immersed in the Ni colloid, and that observed in the Ni–Ag colloid. The lower image shows both colloids as obtained by laser ablation; the upper image, instead, shows metal nanoparticles adhering to the magnetic stir bars. In Figure 1B the two metal targets of nickel and silver are also shown.

**Spectroscopic Characterization.** The UV–visible absorption spectra of the Ni colloid (A) and of Ni–Ag colloid (B) are shown in Figure 2. In particular, the strong band around 400 nm (Figure 2B) corresponds to the plasmon resonance of spheroidal silver nanoparticles. Curves C and D in Figure 2, show the spectral results (practically identical) for the supernatant solutions of the Ni and Ni–Ag samples, respectively, after application of magnetic field. This latter is
performed by introducing a magnetic stir bar into the bottle containing the colloidal suspension. The absence of the spectral features due to nickel and silver (see A and B spectra) indicates that all metal nanoparticles have been removed from the aqueous medium by means of magnetic attraction.

The XPS spectrum (Figure 3) shows that in the colloidal nanoparticles obtained by laser ablation of the nickel target in water, within a depth of about 5 nm, oxidized nickel as Ni(II) is largely predominant with respect to the Ni(0) content, by considering the observed binding energies that closely correspond to those reported in the literature.37 The presence of metallic nickel, however, could play a role in the effect of magnetic attraction, which is observed in the Ni colloid as well as in the bimetallic Ni−Ag colloid.

Raman measurements have been performed for the colloidal samples deposited on an aluminum plate in order to identify the species of oxidized nickel present. Figure 4 shows the spectra registered by micro-Raman instrumentation and 785 nm excitation for different points of the dry film obtained from the deposition of Ni colloid: in the 500−530 cm⁻¹ region a Raman band always occurs, in particular around 505 or 525 cm⁻¹. These spectral features can be attributed to the Ni−O stretching mode of the Ni(II) oxide, in agreement with what reported in the literature.38−42 Actually, a Raman band in the 500−530 cm⁻¹ region could also be attributed to Ni(II) hydroxide, Ni(OH)₂43,44 although it is generally accompanied by two other bands at about 315 and 445 cm⁻¹. As a conclusion, the Raman spectra cannot exclude the concomitant presence of NiO and Ni(OH)₂, also taking into account the fact that two bands are observed at slightly different wavenumbers (505−525 cm⁻¹) for different points of the dry film. A possible formation mechanism of these two species by nickel ablation can be proposed: in the presence of an oxidizing agent such as oxygen dissolved in water, Ni²⁺ is formed, which reacts with the water molecules giving hydroxide, Ni(OH)₂, which in turn is partially transformed by dehydration into oxide, NiO. This hypothesis, however, would require time-resolved measurements for monitoring the fast reactions occurring during the process of laser ablation.

Also for the bimetallic Ni−Ag colloid quite similar Raman bands are observed, to be considered therefore corresponding to the NiO and Ni(OH)₂ species.

Electron Microscopy Analysis. The STEM (scanning/transmission electron microscopy) images of the Ni colloid at low magnification (Figure 5) show spherical nanoparticles immersed in a low-crystallinity matrix with mucilaginous aspect (low contrast). The spherical nanoparticles shown in Figure 5 have diameters varying between 3 and 22 nm, with a mean value of 9.8 ± 0.1 nm (σ = 4.3 nm), but always with crystalline structure, as highlighted by HR-TEM (high-resolution transmission electron microscopy) and SAED (selected area electron diffraction) measurements shown in Figures 6 and 7. This analysis shows interplanar distances corresponding to the planes (111), (200), (220), and (222) of nickel oxide (NiO). By considering these results, it is reasonable to assume the crystalline nanoparticles are made by NiO, whereas the mucilaginous material with low crystallinity is probably formed by nickel hydroxide, Ni(OH)₂.
We have also performed the electron microscopic analysis of the bimetallic Ni−Ag colloid. A quite similar low-contrast matrix is observed (Figure 8), where crystalline metal nanoparticles are interspersed. STEM-EDS (scanning/transmission electron microscopy energy dispersive X-ray spectrometry) measurements (see Figure 9), performed on these nanoparticles, show different situations occurring in the bimetallic colloid: Ag nanoparticles mixed with those of nickel (top panels); heterodimers consisting of Ag nanoparticles on the top of Ni nanoparticles (middle panels); silver clusters deposited on the surface of Ni nanoparticles (bottom panels). In all cases, silver is intimately mixed with the nickel nanoparticles and this explains why silver nanoparticles are not observed in the Ni−Ag colloidal suspension after application of the magnetic field (see Figures 1B and 2). The size distribution of the nanoparticles exhibits a mean value of 13.0 ± 0.1 nm (σ = 6.6 nm) in the range between 4 and 27 nm. The EDS maps of Ni, Ag, and O for the bimetallic colloid, reported in Figure S1 of the Supporting Information, show that nickel is really oxidized, unlike silver.

**Magnetic Properties.** The magnetic characterization of the metal nanoparticles containing only nickel clearly shows the presence of a sharp transition around $T_t = 20$ K, as evidenced by the magnetization data measured as a function of the temperature with a 1 T applied field (inset of Figure 10). Moreover, the hysteresis cycles acquired at decreasing temperatures (Figure 10) display a paramagnetic behavior above $T_t$, while the onset of a magnetic order is observed below this temperature. This behavior can be ascribed to Ni(OH)$_2$, which is ferromagnetic in its $\alpha$-phase with Curie temperature $T_C = 13–23$ K and antiferromagnetic in the $\beta$-phase with the Néel temperature $T_N = 25–26$ K. Due to the reduced size of the system, however, a shift of the characteristic transition temperatures to lower values is often observed and the two phases can be hardly distinguished and identified on the basis of
the magnetic data. The shape of the low-temperature hysteresis loop, for instance, suggests the presence of the ferromagnetic $\alpha$-Ni(OH)$_2$, but, dealing with a nanosized system, it can be also originated by a strongly spin canted magnetic structure of the antiferromagnetically coupled $\beta$-phase.

The metal nanoparticles containing both nickel and silver display a similar behavior with respect to the Ni colloidal sample (Figure 11). The low temperature hysteresis loops of the two samples normalized to the remnant magnetization value are indeed superimposable (inset Figure 11, left panel), the only small difference being in the approach to saturation at high field, which is less pronounced in the Ni sample. In addition, the values of the high field magnetization per Ni gram are very similar for the two samples, being 33.4 and 36.5 emu/g Ni for the Ni and the Ni–Ag samples, respectively. Overall these data suggest that, in the Ni–Ag sample, nickel mostly occurs as hydroxide with a very small amount of Ni(0), while the presence of NiO nanoparticles cannot be unambiguously detected due to the very low signal of this magnetic phase. Since the Ni hydroxide is paramagnetic above $T_c$, the effect of this phase is less evident in the loop recorded at room temperature (Figure 11, right panel) for Ni–Ag, where the weight of the diamagnetic contribution of silver determines a negative slope of the magnetization curve in the high field range.

**SERS Activity.** We have analyzed the SERS response of the Ni–Ag colloid in order to verify the plasmonic characteristics of the bimetallic nanoparticles, in addition to the magnetic properties. Therefore, we have examined the SERS signal of adsorbed adenine ($2.5 \times 10^{-5}$ M concentration), by using the laser excitation at 514.5 nm, a suitable wavelength for the Raman enhancement of the Ag nanoparticles. Adenine has been chosen as the probe molecule in the SERS experiments because it was widely studied spectroscopically and theoretically in previous articles.46,47

Figure 12A shows the SERS spectrum of adenine in the bimetallic Ni–Ag colloid (bottom), compared with that of adenine added with the same concentration to the monometallic Ag colloid obtained by laser ablation (top). These spectra appear very different, in the band positions but especially in the relative intensities. However, the spectrum in
the Ni−Ag colloid is quite similar to that obtained on smooth Ni plate after immersion in adenine−water solution and accurate rinsing with running solvent.48−51 The evident similarity points to the preferential adsorption of adenine on nickel in the Ni−Ag colloid, while the presence of nanosized silver has merely the role of ensuring the electromagnetic enhancement necessary for the observation of the SERS signal. As well as adenine results in being adsorbed on the nickel plate that is oxidized in the surface layer, similarly in the Ni−Ag colloid adenine is adsorbed on the surface of the nickel oxide nanoparticles. By analyzing in more detail the spectra shown in Figure 12A, we note that the SERS spectrum of adenine adsorbed on silver nanoparticles is dominated by a band at about 735 cm−1, corresponding to the ring breathing mode of all the aromatic system.46 In the case of adsorption on NiO nanoparticles, instead, the ring breathing band has intensity comparable to those of the bands recorded at higher frequencies.

We have analyzed this spectral evidence by DFT (density functional theory) calculations, by considering model systems constituted by an adenine molecule linked to an Ag+ adatom, as well as previously performed,47 or to the nickel atom of a NiO molecule. Adenine is known to exist in aqueous solution in two tautomeric forms,52,53 shown in Figure S2 of the Supporting Information, by considering a hydrogen atom bound to the nitrogen atom N7 or N9. In the literature47,54,55 the ring atom N3 of adenine was ascertained by SERS results and DFT calculations to be the preferential candidate to link metal nanoparticles, for both N7 and N9 tautomers. Here, we have considered a model, called Ade(N7)/NiO, with the tautomer N7 interacting with nickel oxide, similarly to that assumed for adenine adsorbed on silver and gold.47 The simulated Raman spectra, shown in Figure 12B, allow reproducing the different intensity patterns of the SERS spectra in Ag and Ni−Ag colloids reported in Figure 12A, with prominent bands corresponding to the observed SERS bands (see Table S1 of the Supporting Information). Normal modes of the Ade(N7)/NiO model are described in Figure S3 of the Supporting Information. The DFT-optimized structures of Figure 13 show that the interaction of adenine with silver involves both rings of the molecule, which instead is linked to nickel oxide only through the atom N3 of the pyrimidinic ring. Another model has been considered, consisting of the tautomer N9 linked to NiO through the N3 atom (Ade(N9)/NiO model), whose

The Ni−Ag colloid is quite similar to that obtained on smooth Ni plate after immersion in adenine−water solution and deposition of silver colloidal nanoparticles (middle). This procedure was previously adopted to obtain the SERS spectra of organic ligands adsorbed on transition metals thanks to the activation due to the dry film of Ag colloidal nanoparticles deposited on smooth metal plates after incubation in the ligand aqueous solution and accurate rinsing with running solvent.48−51 The evident similarity points to the preferential adsorption of adenine on nickel in the Ni−Ag colloid, while the presence of nanosized silver has merely the role of ensuring the electromagnetic enhancement necessary for the observation of the SERS signal. As well as adenine results in being adsorbed on the nickel plate that is oxidized in the surface layer, similarly in the Ni−Ag colloid adenine is adsorbed on the surface of the nickel oxide nanoparticles. By analyzing in more detail the spectra shown in Figure 12A, we note that the SERS spectrum of adenine adsorbed on silver nanoparticles is dominated by a band at about 735 cm−1, corresponding to the ring breathing mode of all the aromatic system.46 In the case of adsorption on NiO nanoparticles, instead, the ring breathing band has intensity comparable to those of the bands recorded at higher frequencies.

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We have obtained stable bifunctional nanoparticles in colloidal suspension by a two-step laser ablation of nickel and silver in pure water, exhibiting both magnetic and plasmonic properties. This procedure avoids the presence of surfactants, organic stabilizers, reducing agents, and reduction byproducts, which could represent an impediment to both the absorption of organic reagents with the surface of the NiO nanoparticles. Magnetic, UV–vis absorption, Raman, and XPS measurements, along with high-resolution TEM analysis, show that such systems are constituted by a low-crystallinity matrix of nickel hydroxide, where nickel oxide nanocrystals are embedded, with silver nanoparticles intimately linked to them. The SERS activity is assessed by the adsorption of adenine, which results in being linked to nickel oxide by a direct interaction of organic reagents with the surface of the NiO nanoparticles. Finally, consideration of the SERS intensities observed in the colloids is necessary. The intensity of the SERS spectrum in laser-ablated Ag colloid could be strongly increased by addition of chloride anions, as recently reported, but our aim here was to compare the SERS spectra obtained in Ag and Ni–Ag colloids without the chloride activation. The SERS spectrum of adenine in the bimetallic colloid appears weaker than that recorded in silver colloid, as immediately deduced from the signal-to-noise ratios. One must consider that in the Ag colloid the SERS intensity depends essentially on the electromagnetic effect due to the silver nanoparticles, to which the molecule is chemically bound. In the bimetallic colloid, instead, the SERS/DFT analysis has showed that the molecule is linked not to silver, but to nickel oxide, which is incapable of promoting enhancement. In this case, the electromagnetic enhancement is ensured by the silver nanoparticles that are located in the immediate vicinity. Therefore, a weaker SERS effect than that found by adsorption on silver is expected.

**CONCLUSIONS**

DFT-optimized structure is also shown in Figure 13, but its simulated SERS profile and calculated frequencies strongly differ from the experimental ones (see Figure 12B and Table S1).

As a conclusion, the DFT approach allows confirming the adsorption of adenine on NiO, as suggested by the SERS measurements, instead of on Ag nanoparticles. This result could be important in view of possible applications of our Ni–Ag nanocomposites in catalytic reactions that provide for the direct interaction of organic reagents with the surface of the NiO nanoparticles. Finally, consideration of the SERS intensities observed in the colloids is necessary. The intensity of the SERS spectrum in laser-ablated Ag colloid could be strongly increased by addition of chloride anions, as recently reported, but our aim here was to compare the SERS spectra obtained in Ag and Ni–Ag colloids without the chloride activation. The SERS spectrum of adenine in the bimetallic colloid appears weaker than that recorded in silver colloid, as immediately deduced from the signal-to-noise ratios. One must consider that in the Ag colloid the SERS intensity depends essentially on the electromagnetic effect due to the silver nanoparticles, to which the molecule is chemically bound. In the bimetallic colloid, instead, the SERS/DFT analysis has showed that the molecule is linked not to silver, but to nickel oxide, which is incapable of promoting enhancement. In this case, the electromagnetic enhancement is ensured by the silver nanoparticles that are located in the immediate vicinity. Therefore, a weaker SERS effect than that found by adsorption on silver is expected.
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