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# Laser Ablation of Silver in Aqueous Solutions of Organic Species: Probing Ag Nanoparticle–Adsorbate Systems Evolution by Surface-Enhanced Raman and Surface Plasmon Extinction Spectra

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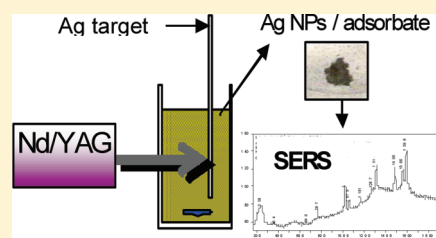
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**ABSTRACT:** Laser ablation (LA) of a Ag target in aqueous solutions of some strongly adsorbing ions resulted in formation of chemically modified Ag nanoparticles (NPs). A prospective development of this approach into a one-pot synthesis of hybrid Ag NPs—organic species systems is conditioned by assessment of the factors affecting the hybrid system formation and stability during LA. In this study, intermittent LA of a Ag target accompanied by fragmentation of growing Ag NPs was carried out in aqueous solutions of 2,2'-bipyridine and/or of a cationic free-base porphyrin with nanosecond laser pulses of 1064 and 532 nm wavelengths. Ag NP/organic adsorbate systems resulting from each of the individual stages of the LA process were probed by SERS (surface-enhanced Raman scattering) and SPE (surface plasmon extinction) spectral measurements. The morphologies of selected systems were visualized by TEM (transmission electron microscopy). The efficiency of Ag NP fragmentation during LA (which corresponds to the efficiency of laser pulse absorption by the NPs) and the rate of the organic molecules' thermal desorption from the surfaces of Ag NPs heated by the laser pulse absorption have been recognized as crucial factors affecting the hybrid system stability.



## 1. INTRODUCTION

Optical responses of plasmonic metal nanoparticles (NPs) based on localized surface plasmon resonances are currently exploited in various branches of plasmonics, such as the development of surface-enhanced Raman scattering (SERS) and single NP spectral sensors, construction of NP-based waveguides, etc.<sup>1,2</sup> To meet the demands of the expansively growing applications, new strategies of plasmonic NP preparation have been developed.<sup>3</sup> Among them, laser ablation (LA) of a Ag target in pure water by high-energy laser pulses has been recognized as a unique method for producing Ag NPs having “chemically pure” surfaces.<sup>4–6</sup> The “purity” actually stems from stabilization of the NPs by OH<sup>−</sup> and HCO<sub>3</sub><sup>−</sup> ions which are the “natural contaminants” of air-exposed aqueous solutions and which are substantially more easily replaced by target adsorbates than the residual ions originating from chemical syntheses of the NPs.<sup>7,8</sup> Another distinct advantage of LA is the possibility to control the NP size and its distribution by physical parameters selected for performing of the process.<sup>9,10</sup> Importantly, not only the outcome but also the mechanisms of LA are critically dependent on laser pulse duration (full width at half-maximum, fwhm) which can span the range of nanoseconds (ns), picoseconds (ps), or femtoseconds (fs).<sup>11</sup> In particular, LA of a Ag target in aqueous ambient performed by ns laser pulses has been found to be

accompanied by Ag NP fragmentation (NF), i.e., by a size reduction of the growing NPs due to laser pulse absorption and a subsequent breaking into fragments. The overall procedure has been denoted as LA/NF.<sup>6,8,12</sup> Laser pulse wavelength and fluence (energy per pulse per unit of the target surface area) are the other important physical parameters affecting the progress and outcome of LA/NF with the ns pulses.<sup>8,13–17</sup>

In addition, it has been demonstrated that the presence of certain chemical species, in particular ions, surfactants, polymers, or a N-base phthalazine, affects the LA/NF process as well.<sup>6,12,17–22</sup> In particular, the presence of strongly adsorbing ions such as chlorides or citrates in the aqueous ablation medium actually leads to a “one-pot” synthesis of purposefully chemically modified NPs.<sup>12,22</sup> All these results point toward a challenging possibility to employ LA/NF for a one-pot synthesis of hybrid systems involving plasmonic metal nanoparticles and functional species, e.g., of dye-modified Ag NPs or Ag NP/polymer or oligomer composites. Nevertheless, this possibility could actually be hampered by several factors, the most serious of which appears

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to be a decomposition of the functional organic species during LA/NF.

In this paper, we focus our attention on assessment of the factors which affect the progress and outcome of LA/NF of Ag in aqueous solutions of organic species which are known for their ability to adsorb spontaneously on Ag NP surfaces. We evaluate these factors from the viewpoint of both (i) formation of the NPs and the stability of the resulting hydrosol in the presence of an organic adsorbate and (ii) preservation/decomposition of the adsorbing organic species in the course of LA/NF. We perform LA/NF by using ns pulses of two different wavelengths, namely, 1064 and 532 nm, and we mutually compare both the progress and outcome of the processes. Employment of the intermittent regime allows us to probe the LA/NF procedures in several (namely, five) stages and to evaluate thus also the effect of the process duration on its outcome. For monitoring of the progress of LA/NF in terms of both (i) and (ii) (as specified above), surface plasmon extinction (SPE) and SERS spectra of resulting Ag NP/adsorbate hydrosol systems were measured after each step of the Ag target irradiation. TEM imaging of selected systems after their deposition was used to support interpretation of the SPE spectra.

The most important criterion of the adsorbing organic species selection was a possibility to readily identify the surface species resulting from their interaction with Ag NP surfaces by means of SERS or SERRS (surface-enhanced resonance Raman scattering) measurements and their interpretation. Therefore, we selected such adsorbates, namely, a neutral N-base 2,2'-bipyridine (bpy) and a cationic free base porphyrin 5,10,15,20-tetrakis(1-methyl-4-pyridiniumyl)-21H,23H porphine ( $H_2TMPyP$ ), for which a detailed characterization of their surface species formed at Ag nanoparticle surfaces has been previously reported.<sup>23,24</sup> In particular, SERS spectral marker bands of the two surface species of bpy,  $Ag^+$ -bpy and  $Ag(0)$ -bpy,<sup>23</sup> and SERRS spectral markers of the three surface species of  $H_2TMPyP$ , i.e., unperturbed  $H_2TMPyP$ ,  $Ag^+$ - $TMPyP$ , and  $Ag(0)$ - $TMPyP$ ,<sup>24</sup> have been identified. Resonance Raman (RR) spectra of  $H_2TMPyP$  have also been reported.<sup>25</sup>

Another point of concern governing the organic species selection was our aim to evaluate the effect of laser pulse absorption by the selected adsorbates and/or their surface species on their stability during LA/NF. Neither bpy nor  $H_2TMPyP$  absorb laser pulses of 1064 nm. On the other hand,  $H_2TMPyP$  and  $Ag^+$ - $TMPyP$  have their Q-absorption bands at 519 and 520 nm, respectively,<sup>26</sup> and the  $Ag(0)$ -bpy surface complex has been found to possess a charge transfer (CT) transition at  $\sim 540$  nm.<sup>27</sup> All these species thus can absorb laser pulses of 532 nm. Concentrations of adsorbates in the aqueous ablation media (namely,  $1 \times 10^{-5}$  M for bpy and  $1 \times 10^{-7}$  M for  $H_2TMPyP$ ) were selected to be sufficiently low to avoid any contribution of the normal Raman signal of free bpy to SERS of adsorbed bpy and of the RR signal of free  $H_2TMPyP$  to SERRS of its surface species.

## 2. EXPERIMENTAL SECTION

**Materials.** Analytical grade chemicals and deionized water were used for all sample preparations. Ag foil (99.99%, 1 mm thickness) and 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21H,23H-porphine ( $H_2TMPyP$ ) were purchased from Aldrich, and 2,2'-bipyridine (bpy) was purchased from Merck.

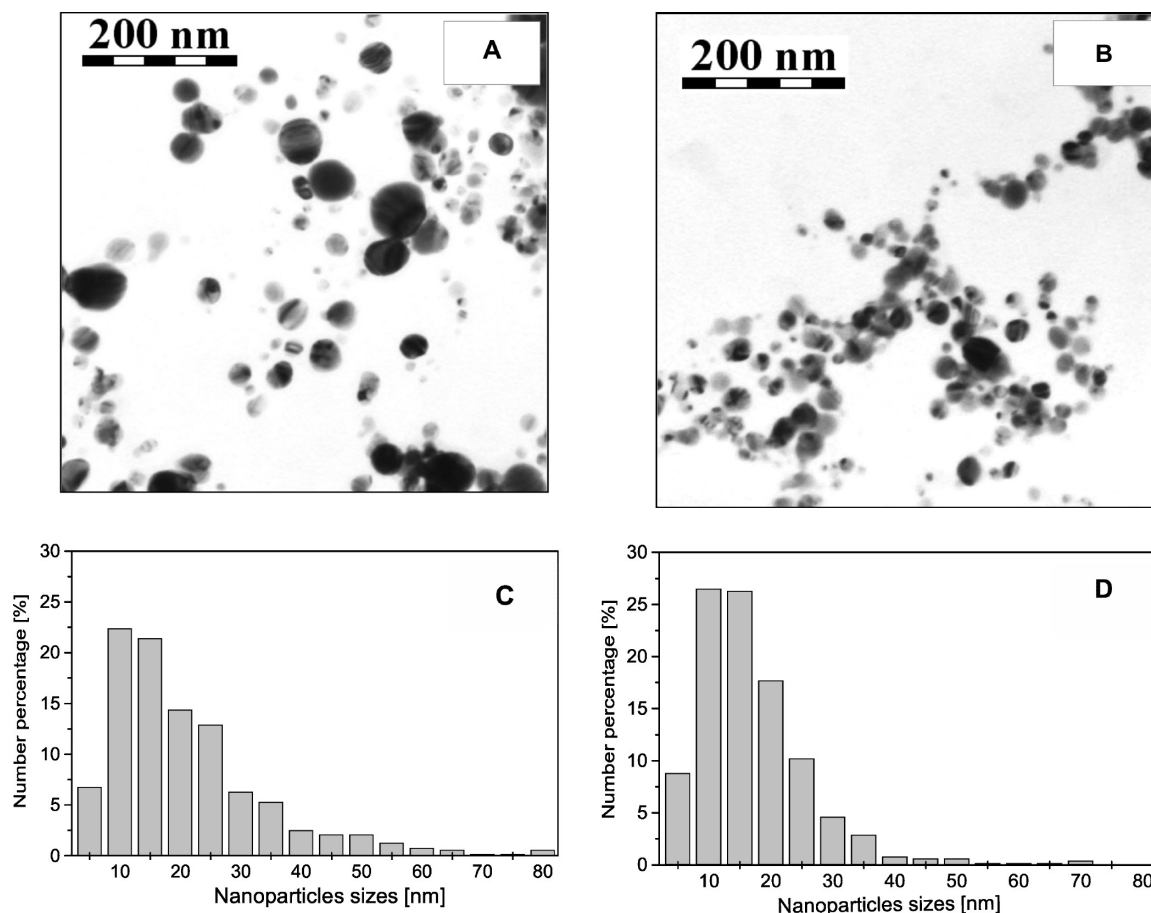
**LA/NF Process.** The Ag foil was immersed in 30 mL of deionized water or  $1 \times 10^{-5}$  M bpy or  $1 \times 10^{-7}$  M  $H_2TMPyP$  aqueous solution placed into a quartz cell was irradiated by focused laser pulses of 1064 (180 mJ/pulse) or 532 nm (60 mJ/pulse) wavelengths. The source was a Nd/YAG laser (Quantel YG58110) with a 10 Hz repetition rate and 20 ns laser pulse duration. A lens (50 mm focal length) was employed for laser beam focusing. Achieved fluences during LA did not exceed 5 and  $0.5 \text{ J/cm}^2$  for 1064 and 532 nm pulses, respectively. The ablation medium was stirred during LA/NF by a magnetically driven stirring bar. The LA/NF procedure was carried out in the intermittent irradiation regime with five irradiations steps of 2, 3, 3, 5, and 7 min. During the dark periods (lasting for ca. 2 min) after each irradiation step, i.e., after 2, 2 + 3, 2 + 3 + 3, 2 + 3 + 3 + 5, and 2 + 3 + 3 + 5 + 7 min of LA/NF, hydrosol samples were collected from the ablation cell and used for SERS and UV/vis (SPE) spectral measurements.

**SERS and SERRS Spectra.** SERS and SERRS spectra of the hydrosol systems placed into a quartz cuvette were measured with a Jobin-Yvon T64000 CCD Raman spectrometer and accumulated for 90 s. SERS spectra of  $AgNP/bpy$  systems were excited with the 514.5 nm excitation line of 200 mW power and those of  $AgNP/H_2TMPyP$  systems with the 488.0 nm line of 160 mW power, both provided by a cw  $Ar^+$  ion laser. The 488.0 nm excitation coincident with the minimum between the Soret (422 nm) and the Q-absorption band (519 nm) of the porphyrin was selected to minimize the molecular resonance contribution to the porphyrin SERRS enhancement and to facilitate detection of possible porphyrin decomposition products. UV/vis spectra were recorded with a Cary 1E spectrophotometer, and their surface-plasmon extinction (SPE) contributions were interpreted on the basis of previously published theoretical and experimental studies.<sup>24,27–30</sup> Samples for TEM imaging were prepared by deposition of a 4  $\mu\text{L}$  droplet of a particular hydrosol system onto a carbon-coated Cu grid followed by its drying in air at room temperature. The TEM images were obtained with a JEOL-JEM 200 CX and a Tecnai F 20 ST transmission electron microscope. For the determination of the particle size distributions (PSD), more than 900 NPs were taken into account from several TEM images of a particular sample.

## 3. RESULTS AND DISCUSSION

**3.1. Morphological Characteristics of Ag NPs, Ag NP/bpy, and  $AgNP/H_2TMPyP$  Hydrosol Systems.** TEM images and particle size distributions (PSDs) of Ag NPs produced by the intermittent LA/NF of Ag in pure water performed with 1064 and 532 nm laser pulses are shown in Figure 1. Their mutual comparison indicates that Ag NP fragmentation (NF), which manifests itself by a reduction of the average NP sizes and narrowing of their PSD, is more efficient with the 532 nm pulses of 60 mJ/pulse (Figure 1B) than with the 1064 nm pulses of 180 mJ/pulse (Figure 1A). The effect of the particular laser pulse wavelengths on the outcome of the intermittent LA/NF in pure water is thus comparable to that reported for the continuous LA/NF (in the same ambient).<sup>8,31</sup>

TEM images of Ag NPs deposited from the hydrosols prepared by the intermittent LA/NF of Ag in  $1 \times 10^{-5}$  M bpy and  $1 \times 10^{-7}$  M  $H_2TMPyP$  aqueous solutions with 1064 and 532 nm laser pulses (with the same energies per pulse as employed for LA/NF in pure water) are shown in Figure 2 (A–D). Their mutual comparison indicates that, for both adsorbates, Ag



**Figure 1.** TEM images and the corresponding PSDs of Ag NPs prepared by intermittent LA/NF in pure water by using 1064 nm (A, C) and 532 nm (B, D) laser pulses.

NPs of substantially smaller sizes are produced in the systems prepared at 532 nm than in those obtained at 1064 nm. A comparison of the TEM images in Figure 2 and those in Figure 1 indicates that the effect of laser pulse wavelengths on the efficiency of Ag NP fragmentation during the intermittent LA/NF in the adsorbate solutions is analogous to that in pure water. Furthermore, an effect of the particular adsorbate on the outcome of the LA/NF can be observed as well. In particular, the presence of bpy during LA/NF appears to have a stabilizing effect on the Ag NPs in the hydrosol, and hence the difference in the sizes of Ag NPs produced at 1064 nm and at 532 nm is even more pronounced in this case (Figure 2 A and C) than for LA/NF in pure water (Figure 1 A and B). By contrast, the presence of H<sub>2</sub>TMPyP leads to destabilization and aggregation of Ag NPs in the final stages of LA/NF at both 1064 and 532 nm (Figure 2 B and D).

**3.2. SPE Spectra of Ag NP/bpy and AgNP/H<sub>2</sub>TMPyP Hydrosol Systems in Successive Stages of Intermittent LA/NF.** Evolutions of the SPE extinction bands in UV/vis absorption spectra of the AgNP/adsorbate systems measured in the dark periods after each of the five irradiation steps at 1064 and 532 nm are shown in Figure 3 A–D. The set of the UV/vis spectra of Ag NP/ $1 \times 10^{-5}$  M bpy systems prepared by LA/NF with 1064 nm pulses (Figure 3A) shows evolution of both the SPE band at  $\sim 400$  nm and of the absorption band of bpy or its surface complex at 281 nm after each step of LA/NF. After the first and the second step, the weak SPE band extends throughout the

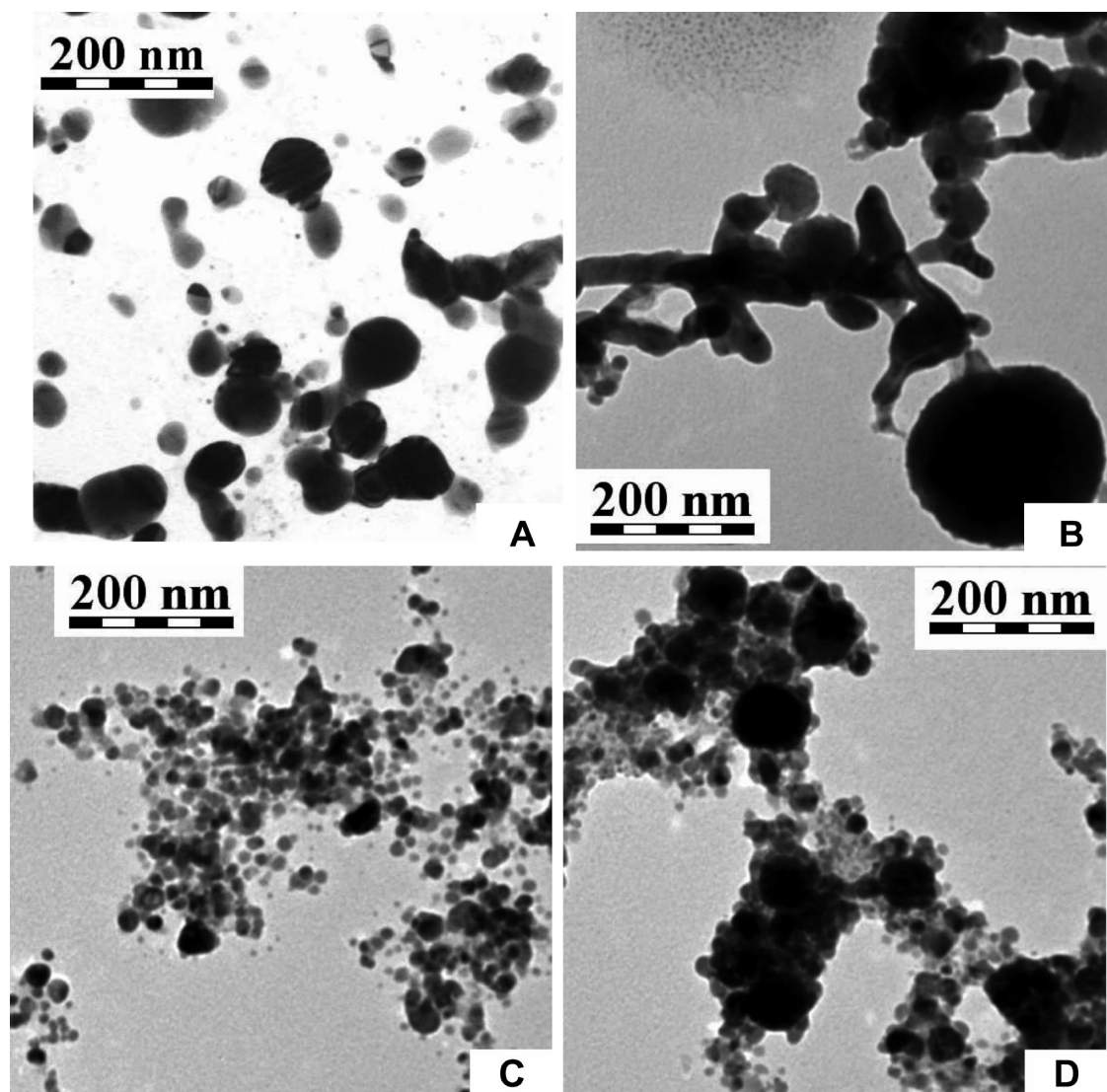
visible region and probably also further into near IR (Figure 3A, curves a and b). Such an SPE band indicates the presence of compact aggregates of fused NPs. Then, in the successive steps, the SPE band grows and becomes gradually narrower due to a systematic decrease of extinction in the 500–800 nm region (Figure 3A, curves c–e), which indicates at least a partial fragmentation of the compact aggregates.

In contrast to that, the SPE spectra of the AgNP/ $1 \times 10^{-7}$  M H<sub>2</sub>TMPyP systems prepared with 1064 nm pulses show a very broad band extending throughout the visible region at all stages of LA/NF (Figure 3B curves a–e). This result indicates a very low efficiency of compact aggregates and/or large NP fragmentation during LA/NF. The somewhat peculiar decrease of the extinction band in the last two stages of LA/NF (without any remarkable changes in its shape) can possibly be explained by sedimentation of Ag NP aggregates.

The SPE spectra of the Ag NP/ $1 \times 10^{-5}$  M bpy system prepared with 532 nm pulses exhibit a weak and broad band only after the first step of LA/NF (Figure 3C, curve a). In the subsequent stages, this band rapidly grows and adopts a narrow shape (Figure 3C, curves b–e). Such a shape indicates the absence of large NPs and NP aggregates resulting from their efficient fragmentation.

For the AgNP/ $1 \times 10^{-7}$  M H<sub>2</sub>TMPyP systems prepared with 532 nm pulses, narrow SPE bands are observed in the spectra measured in the intermediate stages of LA/NF (Figure 3 D, curves b–d), while after completion of the process, broadening



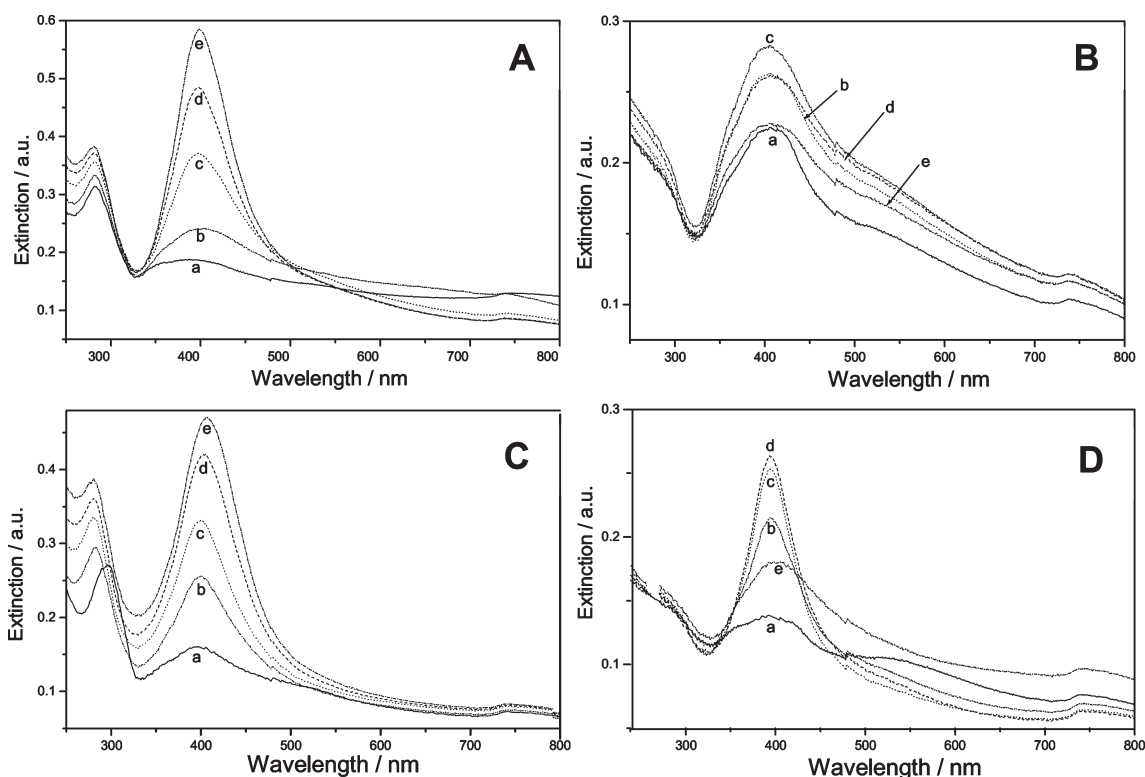


**Figure 2.** TEM images of Ag NPs prepared by intermittent LA/NF with 1064 nm (A, B) and 532 nm (C, D) laser pulses in the aqueous solution of bpy (A, C) and H<sub>2</sub>TMPyP (B, D).

of the SPE band indicates Ag NP aggregation (Figure 3, curve e). The differences between the SPE spectra evolutions of the AgNP/ $1 \times 10^{-7}$  M H<sub>2</sub>TMPyP systems in the intermediate stages of LA/NF at 1064 nm and at 532 nm (Figures 3B and D, curves b–d) can be plausibly explained by a higher efficiency of NF at 532 nm than at 1064 nm. On the other hand, aggregation of Ag NPs at the last stage of LA/NF at 532 nm indicates a severe perturbation of the system. Its nature and origin have been elucidated on the basis of SERS spectral monitoring of this system evolution during LA/NF (Section 3.4).

Finally, the rather narrow and only slightly asymmetric shapes of the SPE curves of AgNP/bpy systems in the final stages of LA/NF (curves e in Figures 3 A and C), on one hand, and the broad SPE curves of the final AgNP/H<sub>2</sub>TMPyP systems (curves e in Figures 3 B and D), on the other, indicate that the presence of bpy has a stabilizing effect on the final hydrosol systems, while the presence of H<sub>2</sub>TMPyP causes their destabilization and aggregation. These conclusions are fully consistent with those drawn in Section 3.1 on the basis of TEM images of the same systems (Figure 2 A–D).

**3.3. SERS Spectral Probing of AgNP/bpy Hydrosol Systems in Successive Stages of Intermittent LA/NF.** SERS spectra of AgNP/bpy ( $1 \times 10^{-5}$  M) systems obtained with 514.5 nm excitation after each of the five steps of the intermittent LA/NF with 1064 and 532 nm pulses are shown in Figures 4 A and B, respectively. The evolution of the SERS spectra of AgNP/bpy systems prepared at 1064 nm shows first an increase (Figure 4A, spectra a and b) and then a slight decrease (Figure 4A, spectra b–e) of the overall SERS signal intensity. On the other hand, SERS spectra intensities of AgNP/bpy systems generated at 532 nm show a systematic decrease (Figure 4B, spectra a–e). The evolutions of SERS signal intensities are most probably related to the efficiency of AgNP fragmentation in each of the systems. In particular, in AgNP/bpy systems prepared at 1064 nm, fragmentation of large NPs is relatively inefficient (see the TEM image of the final system in Figure 2A), hence the SERS signal decrease is relatively small. On the other hand, a more efficient AgNP fragmentation (final TEM in Figure 2 C) is probably responsible for the gradual SERS signal decrease of the AgNP/bpy systems generated at 532 nm. Our explanation is consistent



**Figure 3.** SPE spectra measured after each step ( $a = 2$  min,  $b = 2 + 3$  min,  $c = 2 + 3 + 3$  min,  $d = 2 + 3 + 3 + 5$  min,  $e = 2 + 3 + 3 + 5 + 7$  min) of the intermittent LA/NF performed at 1064 nm (A, B) and 532 nm (C, D) in the presence of bpy (A, C) and  $\text{H}_2\text{TMPyP}$  (B, D).

with the earlier results of SERS spectral testing of AgNP hydrosols prepared by LA/NF. It showed that larger NPs produced by LA/NF (in water) at 1064 nm are more efficient SERS substrates than the small AgNPs resulting from the more efficient NF during LA/NF at 532 nm.<sup>14</sup>

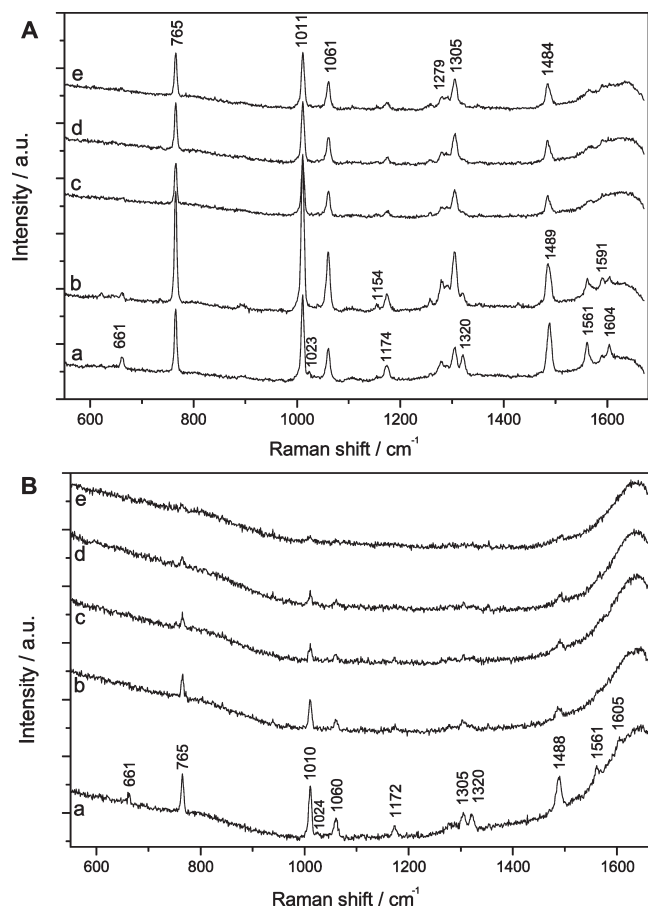
Assignment of the SERS spectral bands based on the pure component spectra of  $\text{Ag}^+\text{-bpy}$  and  $\text{Ag(0)-bpy}$ <sup>23</sup> reveals that spectral marker bands of both  $\text{Ag}^+\text{-bpy}$  (1011, 1305  $\text{cm}^{-1}$ ) and  $\text{Ag(0)-bpy}$  (661, 1023, 1320, 1561, 1605  $\text{cm}^{-1}$ ) are found in the first two spectra (a and b) in Figure 4 A and in the first spectrum (a) in Figure 4B. By contrast, only the  $\text{Ag}^+\text{-bpy}$  bands are present in all the subsequent spectra of both series (Figure 4 A, spectra c–e, and B, spectra b–e). It should be noted that the SERS spectral bands at 765, 1061, 1174, 1279, and 1489  $\text{cm}^{-1}$  are common to both surface species. No other bands attributable to a decomposition product of bpy have been observed. SERS spectral probing thus provides evidence for formation of a small fraction of  $\text{Ag(0)}$  adsorption sites, in addition to the more abundant  $\text{Ag}^+$  adsorption sites, on the surfaces of AgNPs in early stages of LA/NF. It is worth mentioning here that only  $\text{Ag}^+$  adsorption sites have been encountered on surfaces of AgNPs prepared by either LA/NF<sup>14</sup> or reduction of silver nitrate by sodium borohydride.<sup>23</sup> On the other hand,  $\text{Ag(0)}$  adsorption sites stabilized by bpy into  $\text{Ag(0)-bpy}$  have been detected on surfaces of AgNPs (by SERS at 514.5 nm excitation) provided that bpy has been present during the chemical reduction of silver nitrate by sodium borohydride. In that case, observation of  $\text{Ag(0)-bpy}$  has been explained by formation of  $\text{Ag(0)}$  sites in the strongly reducing ambient.<sup>23</sup> Furthermore, it has been shown that once the  $\text{Ag(0)}$  sites are stabilized by bpy the resulting  $\text{Ag(0)-bpy}$  species is quite resistant against oxidation.<sup>23</sup> By

contrast, in the absence of a stabilizing adsorbate,  $\text{Ag(0)}$  sites are prone to oxidation.<sup>32</sup> The rarity of the  $\text{Ag(0)}$  sites' occurrence prompted us to seek at least a tentative explanation for their appearance at the early stage and disappearance at the later stages of LA/NF.

Concerning the  $\text{Ag(0)}$  site formation, we propose tentatively that they originate during AgNP growth from the primary products of LA, which are Ag atoms,  $\text{Ag}_n^+$  species, and ejected electrons, as well as larger metal clusters<sup>31</sup> and, in the presence of bpy, are readily stabilized by  $\text{Ag(0)-bpy}$  surface species formation. Concerning the disappearance of this species in the later stages of LA/NF we have considered the following possibilities: (i) a spontaneous oxidation of  $\text{Ag(0)-bpy}$  to  $\text{Ag}^+\text{-bpy}$  in air, (ii) photodecomposition of  $\text{Ag(0)-bpy}$  by laser pulse absorption, followed by oxidation of adsorbate-free  $\text{Ag(0)}$  to  $\text{Ag}^+$ , and (iii) thermal decomposition of  $\text{Ag(0)-bpy}$  resulting from heating of AgNP surfaces by absorption of laser pulses by the NPs, followed by the  $\text{Ag(0)}$  to  $\text{Ag}^+$  free-site oxidation.

For evaluation of the first possibility (i), we allowed the AgNP/bpy systems obtained after 2 min of LA/NF to age in air for 30 min (approximately the time of the overall intermittent LA/NF procedure). Then, their SERS spectra have been measured and compared to the SERS spectra of the corresponding systems prior to their aging (Figure 5). Since the relative intensity ratios of the 1320  $\text{cm}^{-1}$  band of  $\text{Ag(0)-bpy}$ /1305  $\text{cm}^{-1}$  of  $\text{Ag}^+\text{-bpy}$  do not principally change with the system aging (Figures 5A and B, spectra a and b), a spontaneous oxidation cannot be the major mechanism responsible for  $\text{Ag(0)-bpy}$  signal disappearance.

Furthermore, since the  $\text{Ag(0)-bpy}$  spectral bands vanish during LA/NF at both 1064 and 532 nm (Figure 4 A and B), while the  $\text{Ag(0)-bpy}$  surface complex can absorb only the 532 nm

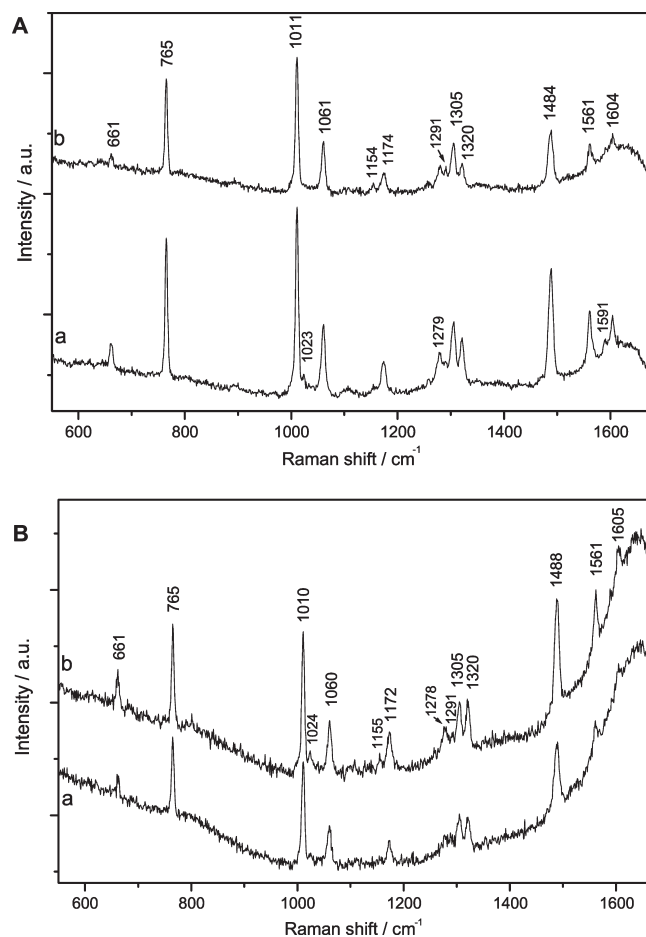


**Figure 4.** Evolution of the SERS spectra ( $\lambda_{\text{exc}} = 514.5$  nm) of AgNP/bpy systems throughout the stages (a = 2 min, b = 2 + 3 min, c = 2 + 3 + 3 min, d = 2 + 3 + 3 + 5 min, e = 2 + 3 + 3 + 5 + 7 min) of intermittent LA/NF performed at 1064 nm (A) and 532 nm (B).

pulses (owing to excitation of a CT transition at ca. 540 nm<sup>27</sup>), (ii) the photodecomposition through absorption of laser pulses is not a major mechanism of Ag(0)-bpy decomposition, either.

Therefore, the most probable mechanism is (iii) the thermal decomposition of Ag(0)-bpy surface species due to the heating of AgNPs by absorption of laser pulses prior to their fragmentation, followed by the Ag(0) to Ag<sup>+</sup> free-site conversion. This conversion can proceed either by a spontaneous oxidation of the adsorbate-free Ag(0) (owing to a slow diffusion of bpy molecules to the fragmented NPs) or possibly also by a positive charging of AgNPs due to Ag<sup>+</sup> formation (accompanied by electron ejection) during NF (ref 13, in particular Figure 9 therein).

In summation, we propose that Ag(0) adsorption site formation and stabilization is associated chiefly with the processes progressing in the aqueous solution in the aftermath of LA, while their destabilization and oxidation with the thermally induced processes on AgNP surfaces accompanying NF. It is now quite well established<sup>16,33</sup> that at the early stage of LA/NF the efficiency of LA is maximal, while at later stages, it decreases due to the absorption of laser pulses by the already formed AgNPs in the hydrosol prior to their impact on the Ag target. By contrast, the extent of NF increases with the increasing number of light-absorbing NPs. Therefore, the efficiency of Ag(0) adsorption site formation and stabilization is expected to be higher in the early stage of LA/NF, while in the later stages, their abundance is



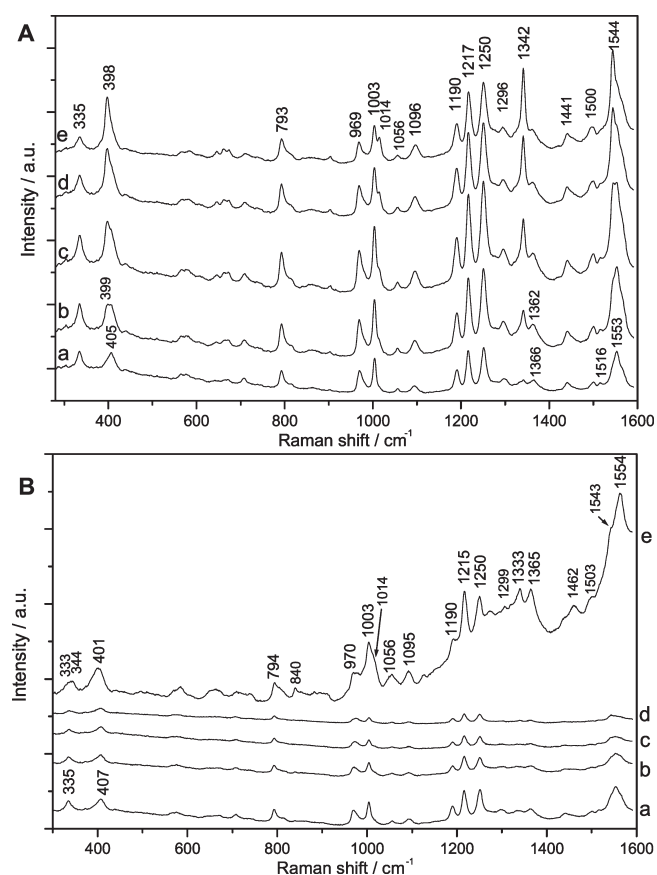
**Figure 5.** SERS spectra ( $\lambda_{\text{exc}} = 514.5$  nm) of AgNP/bpy systems prepared by LA/NF for 2 min at 1064 nm (A) and 532 nm (B), measured immediately (a) and 30 min after the preparation (b).

expected to decrease substantially through both the decreasing efficiency of their formation and the increasing efficiency of their destruction.

Finally, our results indicate that the efficiencies of NF and of Ag(0) site destruction are, indeed, mutually interrelated. In particular, SPE spectral probing has shown an efficient NF after the third step of LA/NF at 1064 nm (Figure 3A, curve c), while the same effect was achieved already in the second step of LA/NF at 532 nm (Figure 3C, curve b). Analogously, the SERS signal of Ag(0)-bpy virtually disappears after the third step of LA/NF at 1064 nm (Figure 4A, spectrum c) but already after the second step at 532 nm (Figure 4B, spectrum b).

**3.4. SERS Spectral Probing of AgNP/H<sub>2</sub>TMPyP Hydrosol Systems in Successive Stages of Intermittent LA/NF.** Evolution of the SERS spectra of the AgNP/H<sub>2</sub>TMPyP ( $1 \times 10^{-7}$  M) system throughout the stages of LA/NF with 1064 nm laser pulses is depicted in Figure 6A. After the 2 min first step of LA/NF, only the H<sub>2</sub>TMPyP spectral marker bands (335, 405, 969, 1003, 1366, and 1553 cm<sup>-1</sup>) are detected in the SERS spectrum of the system (Figure 6A, spectrum a), together with the 794, 1190, 1217, 1250, 1296, 1441, and ~1500 cm<sup>-1</sup> bands common to both the free base and the metalated porphyrin. In the subsequent stages of LA/NF, SERS spectral marker bands of AgTMPyP (398, 1014, 1342, 1544) appear (Figure 6A, spectrum b), and their relative contribution to the overall SERS signal





**Figure 6.** Evolution of the SERRS spectra ( $\lambda_{\text{exc}} = 488$  nm) of AgNP/ $\text{H}_2\text{TMPyP}$  systems throughout the stages ( $a = 2$  min,  $b = 2 + 3$  min,  $c = 2 + 3 + 3$  min,  $d = 2 + 3 + 3 + 5$  min,  $e = 2 + 3 + 3 + 5 + 7$  min) of intermittent LA/NF performed at 1064 nm (A) and 532 nm (B).

gradually increases (Figure 6A, spectra c–e). Such an evolution is typical for the progress of  $\text{H}_2\text{TMPyP}$  metalation on the AgNP surface.<sup>6,24,26,34</sup>

By contrast, only  $\text{H}_2\text{TMPyP}$  marker bands are detected throughout the first four stages ( $2 + 3 + 3 + 5$  min.) of LA/NF with 532 nm pulses (Figure 6B, spectra a–d). After the last stage of LA/NF, some spectral features of a metalated form of the porphyrin appear in the spectrum in addition to the bands of  $\text{H}_2\text{TMPyP}$ , superimposed on the broad background bands attributable to amorphous carbon (Figure 6B, spectrum e, and ref 35). Their occurrence signifies a partial metalation as well as a partial decomposition of the porphyrin molecules.

The substantial differences between evolutions of AgNP/porphyrin systems during LA/NF with the 1064 and 532 nm pulses (Figure 6) are not limited to the SERRS spectra, but manifest themselves in their SPE spectral features as well (Figure 3B and D). In particular, the presence of large AgNPs and/or aggregates during LA/NF with 1064 nm pulses (reflected by broad and asymmetric SPE bands in Figure 3B) not only signifies a very low degree of their fragmentation but also explains observation of the good quality porphyrin SERRS signals in Figure 6A. In contrast to that, the absence of such large NPs or aggregates during the first four stages of LA/NF with 532 nm pulses (Figure 3D curves a–d) signifies their efficient fragmentation, which, in turn, is responsible for low intensities of the porphyrin SERRS signals detected (Figure 6B, spectra a–d). On the other

hand, AgNP aggregation (witnessed by the TEM image in Figure 2D and the broad SPE curve e in Figure 3D) is probably responsible for the observed porphyrin SERRS signal increase in spectrum e (Figure 6B).

Furthermore, to shed more light on both the porphyrin molecule stability under pulsed laser irradiation and the rate of its metalation on AgNP surfaces, two series of control experiments (with 1064 and 532 nm pulses) have been performed. All steps of the intermittent LA/NF (in pure water) and the irradiation of the  $1 \times 10^{-7}$  M  $\text{H}_2\text{TMPyP}$  aqueous solution were performed separately but under the same irradiation conditions and regime. After each irradiation step, the AgNP hydrosol and the porphyrin solution were mixed together, and SERS/SERRS spectra of the resulting systems were measured (Figure 7) and compared to those obtained after each step of LA/NF (Figure 6).

In the series of spectra in Figure 7A obtained by the control experiment with 1064 nm pulses, we observe almost entirely the marker bands of  $\text{H}_2\text{TMPyP}$  with only very weak traces of the strongest  $1342\text{ cm}^{-1}$  marker band of AgTMPyP (while its other markers are absent). This result indicates that the ca. 1 min delay from system preparation to its SERS spectral measurement is too short to achieve a spectrally detectable degree of the porphyrin metalation, in accord with the previously published papers regarding the rates of this porphyrin metalation in systems with Ag NP hydrosols preprepared by LA/NF.<sup>6,26,34</sup>

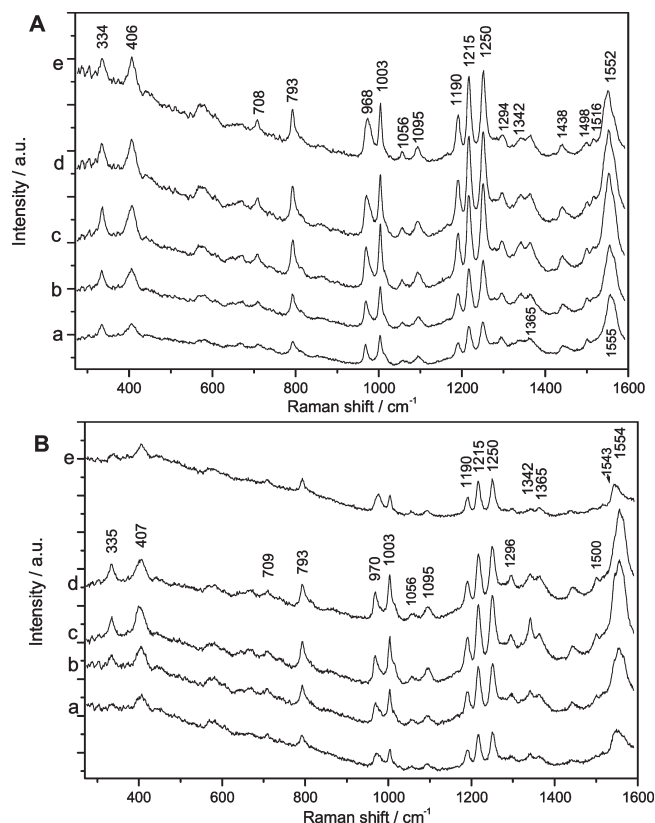
A mutual comparison of the series of SERRS spectra in Figures 6A and 7A and, in particular, of both the final spectra e indicates that an efficient porphyrin metalation (i.e., AgTMPyP formation) is achieved only provided that the porphyrin is present during the LA/NF procedure (lasting, in summation, for ca. 30 min) (Figure 6A, spectra a–e). Additionally, the systematic progress of the porphyrin metalation indicates that the desorption–readsorption processes thus do not play an important role during LA/NF at 1064 nm. This result, in turn, is consistent with the already mentioned very low extent of AgNPs and their aggregate fragmentation (Figure 3B).

In contrast to that, the porphyrin metalation is completely hindered during the first four stages of LA/NF with 532 nm pulses (Figure 6B), most probably due to the desorption–readsorption processes which accompany the efficient AgNP and aggregate fragmentation witnessed by the SPE bands shown in Figure 3D (curves a–d). Importantly, no decomposition of  $\text{H}_2\text{TMPyP}$  molecules to amorphous carbon has been detected throughout these first four stages of LA/NF.

In relation to the porphyrin decomposition observed in the last step of LA/NF (Figure 6B, spectrum e), the corresponding control experiment (Figure 7B, spectrum e) shows no additional SERS/SERRS spectral band attributable to a decomposition product. This result indicates that the porphyrin decomposition (i) does not occur in the course of the SERRS spectral measurement and (ii) proceeds only when the porphyrin irradiation with 532 nm pulses is performed in the presence of AgNPs.

One of the possible causes of the porphyrin decomposition could be metalation of  $\text{H}_2\text{TMPyP}$  on AgNP surfaces (i.e., AgTMPyP formation), which, in turn, can substantially affect the progress of the thermally induced porphyrin desorption from the AgNPs. The reason for that originates from the principal differences in attachment of  $\text{H}_2\text{TMPyP}$  and AgTMPyP toward the AgNP surface. While the  $\text{H}_2\text{TMPyP}$  molecular ions are attached to the AgNP surface via an electrostatic interaction between the four positively charged pyridiniumyl side groups and the negatively charged outer parts of the electric double layer





**Figure 7.** Evolution of the SERRS spectra ( $\lambda_{\text{exc}} = 488$  nm) of a control experiment in which AgNPs prepared separately by the intermittent LA/NF in pure water were mixed together with  $\text{H}_2\text{TMPyP}$  irradiated in aqueous solution using the same irradiation regime as that employed for LA/NF ( $a = 2$  min,  $b = 2 + 3$  min,  $c = 2 + 3 + 3$  min,  $d = 2 + 3 + 3 + 5$  min,  $e = 2 + 3 + 3 + 5 + 7$  min). Irradiation was performed at 1064 nm (A) and 532 nm (B).

enveloping AgNPs, AgTMPyP is formed by incorporation of Ag into the center of the porphyrin macrocycle due to attachment of  $\text{H}_2\text{TMPyP}$  to  $\text{Ag}^+$  adsorption sites.<sup>6,24,26,34</sup> Desorption of  $\text{H}_2\text{TMPyP}$  from the heated particle surface is, apparently, fast enough to prevent its decomposition (Figure 6B, spectra a–d). By contrast, in the case of AgTMPyP surface species, bound directly to the AgNP surface with the flat-lying porphyrin macrocycle in close contact with the surface, the desorption energy can be too high to enable a rapid desorption of the porphyrin from the heated particle prior to its decomposition to amorphous carbon (Figure 6B, spectrum e).

Finally, the drastic changes of the aggregation state of AgNPs as well as of the porphyrin metalation and stability encountered in the AgNP/porphyrin systems during the last, fifth stage of LA/NF (of 7 min duration) at 532 nm are tentatively explained by the following sequence of events: (i) mostly small AgNPs are present in the system after the preceding four stages of LA/NF involving an efficient NF, as witnessed by a narrow and symmetric curve d in Figure 3. (ii) Since these NPs do not absorb 532 nm pulses efficiently (due to a low extinction at this wavelength in curve d, Figure 3), the extent of NF in the last and longest fifth stage of LA/NF is low. Therefore, the desorption–readsorption processes do not play an important role any longer (in contrast to 1–4 stages), and the porphyrin metalation proceeds. (iii) The direct adsorption of some of the porphyrin molecules (documented

by the residual AgTMPyP spectral features detection, Figure 6B, spectrum e) leads to destruction of the electric bilayer around the NPs and causes their aggregation (witnessed by the TEM image in Figure 2D and by the broad curve e in Figure 3D). (iv) The resulting aggregates (Figure 2D) do absorb laser pulses (as documented by their relatively high extinction at this wavelength, curve e in Figure 3D), which, in turn, causes heating of the AgNP surface. (v) The strongly bound (and hence slowly desorbing) AgTMPyP surface species thermally decomposes to amorphous carbon on the surfaces of aggregated AgNPs upon heating (as witnessed by the broad bands of amorphous carbon forming the background of spectrum e in Figure 6B).

#### 4. CONCLUSIONS

The combined SERS, SPE, and TEM probing revealed that the heating effect caused by absorption of the ns laser pulses by AgNPs and/or their aggregates is the crucial factor influencing preservation/decomposition of organic species during LA/NF of Ag carried out in their aqueous solutions. In particular, it has been demonstrated that the 1064 nm wavelength is a better choice for LA/NF in the organic adsorbate presence than the 532 nm one. At the former wavelength, the less efficient light absorption by AgNPs (and hence also NF) reduces the extent of the heating effects and the risks of adsorbate decomposition.

Nevertheless, stable systems can, under certain conditions, result from LA/NF at 532 nm as well. In that case, the rate of adsorbate desorption upon heating emerges as the most important adsorbate-dependent factor. This, in turn, depends on the adsorbate–AgNP surface interaction and the particular surface species formation. In particular, the preservation of a cationic porphyrin  $\text{H}_2\text{TMPyP}$  under the regime of the efficient AgNP fragmentation during the first four stages of LA/NF at 532 nm indicates a good chance for survival of other cationic species electrostatically bound to the negatively charged outer part of the electric double layer enveloping AgNPs. Importantly,  $\text{H}_2\text{TMPyP}$  molecules remained intact despite the fact that they themselves absorb at 532 nm. Similarly, no bpy decomposition products were detected during LA/NF involving the efficient NF.

On the other hand, formation and decomposition of AgTMPyP in the very last stage of the intermittent LA/NF at 532 nm demonstrates that the change in the surface–adsorbate interaction from the electrostatic bonding via an anionic spacer to the direct adsorption dramatically alters the organic species stability.

Finally, the evolution of the system with  $\text{H}_2\text{TMPyP}$  during LA/NF at 532 nm indicates that surface–adsorbate interactions and, in their consequence, also the system morphology and the surface-species stability, can vary in the course of LA/NF. Therefore, the duration of the LA/NF process can also represent an important factor affecting its final outcome. With this knowledge at hand, stable AgNP/ $\text{H}_2\text{TMPyP}$  nanohybrid systems can be prepared simply by limiting the intermittent LA/NF process at 532 nm to the first four stages.

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