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## Controlled joining of Ag nanoparticles with femtosecond laser radiation

H. Huang,<sup>1,a)</sup> L. Liu,<sup>1,2</sup> P. Peng,<sup>1</sup> A. Hu,<sup>1,b)</sup> W. W. Duley,<sup>3</sup> and Y. Zhou<sup>1</sup>

<sup>1</sup>Centre for Advanced Materials Joining, Department of Mechanical & Mechatronics Engineering, University of Waterloo, Ontario N2L 3G1, Canada

<sup>2</sup>Department of Mechanical Engineering, Tsinghua University, 100084, China

<sup>3</sup>Department of Physics & Astronomy, University of Waterloo, Ontario N2L 3G1, Canada

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We show that it is possible to tailor the gap separation and interface geometry between adjacent Ag nanoparticles (NPs) by controlling fluence when irradiating with pulses from a fs laser. Unirradiated samples extracted from aqueous solution consist of networks of Ag NPs coated with polyvinylpyrrolidone (PVP). At low laser fluence, bonding between NPs occurs via the formation of an intervening hydrogenated amorphous carbon ( $\alpha$ -C:H) layer resulting from the laser-induced decomposition of PVP. This occurs when electrons are emitted at hot-spots created by the trapping of plasmons. The thickness of the  $\alpha$ -C:H layer determines the minimum separation between NPs. Ag NPs with different contact geometries can be produced by irradiation of the networks in solution at fluences exceeding the threshold for the formation of  $\alpha$ -C:H. At fluences between 200 and 380  $\mu\text{J}/\text{cm}^2$ , the  $\alpha$ -C:H interface layer is replaced with a metallic neck. Surface enhanced Raman scattering (SERS) has been used to quantify the electromagnetic field enhancement in joined NP samples. We find that Ag NPs bonded by  $\alpha$ -C:H and exhibiting a narrow gap possess the highest SERS enhancement. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4770476>]

### I. INTRODUCTION

Devices containing Ag and Au nanoparticles (NPs) have attracted much interest due to their unique surface plasmon resonance (SPR) properties which can lead to enhanced fluorescence,<sup>1</sup> Raman scattering,<sup>2</sup> and hyper-Raman scattering<sup>3</sup> for applications in molecular diagnostics, biomedical devices, and other nano-structured detectors. Networks of NPs are particularly effective in these applications because they can produce a large enhancement of SPR.<sup>4</sup> Many chemical methods have been reported as effective for the preparation of NPs networks with good SPR enhancement,<sup>5–7</sup> but most of these techniques generally involve several individual steps that add additional complexity. In these preparation techniques, organic links also tend to prevent analyte molecules from entering active surface sites. Link molecules are often characterized by weak bond strength leading to variability in surface enhanced Raman scattering (SERS) enhancement, which limits their use in many applications. In a previous study, we have demonstrated that irradiation with fs laser pulses is a convenient way of producing welds between NPs.<sup>8</sup> Welded NPs created using fs laser irradiation have good bond strength and better SPR enhancement than in samples containing single NPs. As fs irradiation at low fluence does not alter the shape of NPs,<sup>9</sup> welding with fs laser pulses is better suited than conventional thermal processing<sup>10–14</sup> to the fabrication of NPs with specific shapes optimized to generate tunable plasmon properties. However, it has been found in numerical simulations that welded NPs are still not the most efficient structures for SPR enhancement.<sup>15</sup> These calculations indicate that dimers with a narrow interparticle gap are capable of producing the highest local elec-

tromagnetic field enhancements. In this paper, we show that it is possible to form such structures by the irradiation of Ag NPs in aqueous solution with fs laser pulses under controlled conditions. We investigate the role played by pulse fluence on the subsequent interface geometry between pairs of Ag NPs and have used SERS techniques to evaluate SPR enhancement with different contact geometries.

### II. EXPERIMENTAL

Ag NPs having particle sizes between 30 and 50 nm were introduced into an aqueous solution of polyvinylpyrrolidone (PVP) as reported previously.<sup>13</sup> This solution, containing PVP coated Ag NPs, was diluted to 0.2 mM to obtain a sample of well dispersed NPs. 5 ml of this dilute Ag NP solution was then placed into a quartz cell and irradiated for 20 min with 35 fs 800 nm laser pulses at 1 kHz. The laser was manufactured by Coherent, Inc. The spot diameter of the laser beam at the focus inside the quartz cell was 10 mm. Pulse fluences of 95, 200, and 380  $\mu\text{J}/\text{cm}^2$  were obtained by attenuating the beam with neutral density filters (Thorlab, Inc.). Scanning electron microscopy (SEM, LEO 1530 Zeiss, Germany) and transmission electron microscopy (TEM, JEOL-JEM-2010F) were used to analyze NP morphology. Raman spectra of pure PVP and Ag NPs before and after irradiation were obtained after deposition on cleaned Si substrates; while a 1 mM adenine solution was used to evaluate SERS enhancement by Ag NPs before and after irradiation. The wavelength of the exciting laser for Raman and for excitation of SERS spectra was 488 nm.

### III. RESULTS AND DISCUSSIONS

Fig. 1 shows TEM and HRTEM morphologies of Ag NPs after irradiation for 20 min at different fluence. It can be seen

<sup>a)</sup>Electronic mail: h57huang@uwaterloo.ca.

<sup>b)</sup>Electronic mail: a2hu@uwaterloo.ca.

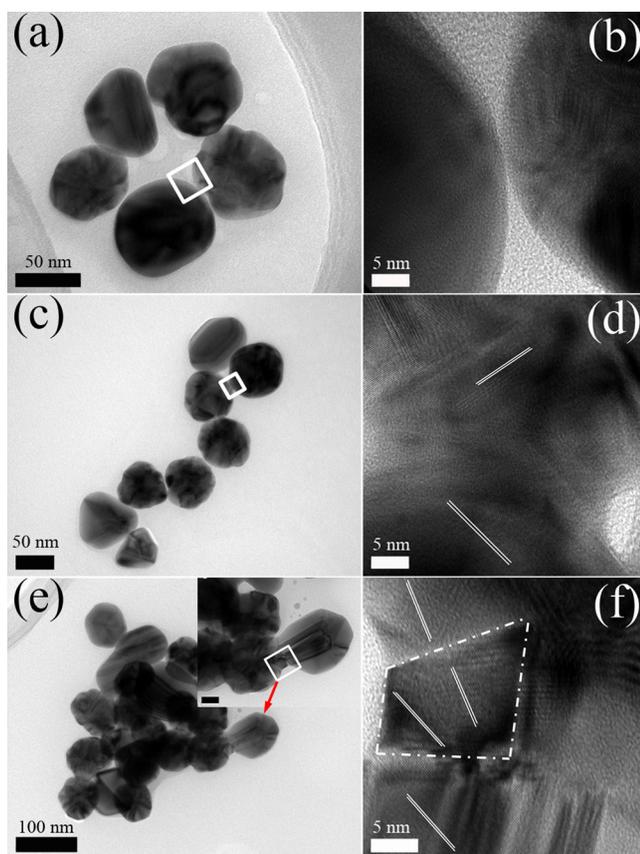


FIG. 1. TEM (left) and HRTEM (right) images of Ag NPs irradiated by fs laser with different pulse fluence for 20 min: (a) and (b)  $90 \mu\text{J}/\text{cm}^2$ , (c) and (d)  $200 \mu\text{J}/\text{cm}^2$ , (e) and (f)  $380 \mu\text{J}/\text{cm}^2$ . The scale in the inset figure is 20 nm.

that irradiation results in the formation of Ag NP networks (Figs. 1(a), 1(c), and 1(e)), but that the shape of individual particles is not significantly affected by this process. Figs. 1(a) and 1(b) show that after irradiation at a fluence of  $95 \mu\text{J}/\text{cm}^2$ , Ag NPs was separated by an  $\sim 0.5 \text{ nm}$  narrow gap and they appear to be bonded by a carbonaceous shell. When the fluence increased to 200 and  $380 \mu\text{J}/\text{cm}^2$  (Figs. 1(c) and 1(e)), part of the inter-particle gaps was replaced by necks. HRTEM images show that these necks are metallic, acting as bridges between individual Ag NPs, and widen as the fluence increase (Figs. 1(d) and 1(f)). The mechanisms of the coalescence between NPs, e.g., on how the neck layers form and how the coalescing atomic planes align to those of the NPs, have been discussed extensively in the literatures.<sup>16,17</sup> It appears in this work that neck layers can form (see the dashed region in Fig. 1(f)) where part of the planes are aligned almost parallel to those in the above NP while the others parallel to those in the bottom NP. The formation mechanism of this configuration, which has not been reported in literature, needs further studies. But, it is clear from the above observations that the separation between Ag NPs (i.e., inter-particle distance) can be controlled by adjusting laser fluence and that laser irradiation of NPs in solution may be a useful technique for tailoring the properties of Ag NP networks.

Raman spectra of Ag NPs before and after fs laser irradiation were obtained after deposition on a clean Si substrate (Fig. 2). Fig. 2(a) shows the Raman spectrum of a sample prepared from NPs prior to irradiation. Spectral features at

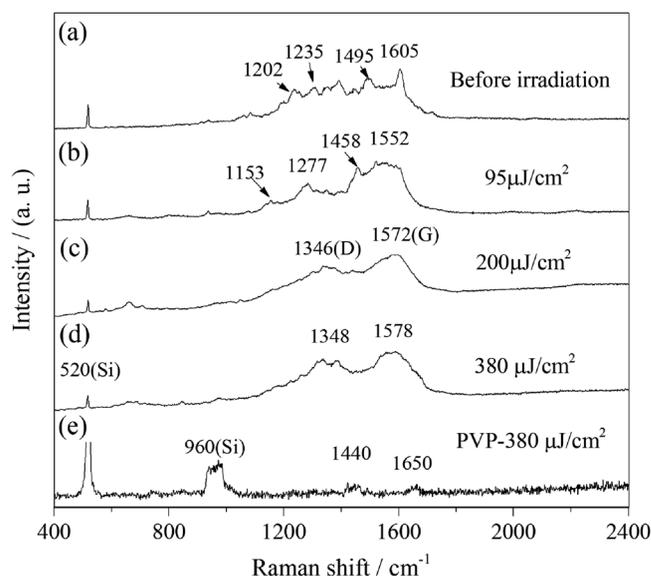


FIG. 2. Raman spectra of Ag NPs and PVP in aqueous solution before and after irradiation with fs laser pulses: (a) NPs before irradiation, (b) NPs after irradiation at  $95 \mu\text{J}/\text{cm}^2$ , (c) NPs after irradiation at  $200 \mu\text{J}/\text{cm}^2$ , (d) NPs after irradiation at  $380 \mu\text{J}/\text{cm}^2$ , (e) pure PVP solution after irradiation at  $380 \mu\text{J}/\text{cm}^2$ .

$1202$ ,  $1235$ ,  $1495$ , and  $1605 \text{ cm}^{-1}$  are indicative of the presence of PVP<sup>18</sup> which forms a coating on each NP. After irradiation at a fluence of  $95 \mu\text{J}/\text{cm}^2$ , peaks associated with the stretching vibration of  $\text{sp}^2$ -bonded carbon (the “G” peak) appears at  $1552 \text{ cm}^{-1}$  together with bands at  $1153$ ,  $1277$ , and  $1458 \text{ cm}^{-1}$  attributable to trans-polyacetylene chains.<sup>19–23</sup> These spectral features indicate that  $\alpha\text{-C:H}$  is created by irradiation of the Ag PVP solution. The Raman spectra in Figs. 2(c) and 2(d) show that the G peak shifts to  $1572$  and  $1578 \text{ cm}^{-1}$ , while another feature “D” peak arising from  $\text{sp}^2$ -bonded carbon in defect sites in amorphous carbon ( $\alpha\text{-C}$ ) appears at  $1346$  and  $1348 \text{ cm}^{-1}$  in samples irradiated at fluences of 200 and  $380 \mu\text{J}/\text{cm}^2$ , respectively. The amplitude ratio of the D and G peaks ( $I_D/I_G$ ) is also found to increase with fluence indicating that the C/H ratio and structural order are enhanced in  $\alpha\text{-C:H}$  under these conditions.<sup>24</sup>

Since PVP is only weakly absorbing at  $800 \text{ nm}$ , it is unlikely that PVP can be decomposed by irradiation in aqueous solution at low fluence.<sup>25</sup> The Raman spectrum of an aqueous solution of PVP after irradiation can be seen in Fig. 2(e) and is characterized by the C=O, C-N stretching bands<sup>26</sup> of the PVP molecule. No spectral features of  $\alpha\text{-C:H}$  or  $\alpha\text{-C}$  are detected indicating that PVP is not decomposed under low fluence conditions. We, therefore, attribute the formation of  $\alpha\text{-C:H}$  and  $\alpha\text{-C}$  to thermal decomposition of PVP at the surface of Ag NPs.

To understand the mechanism for the decomposition of PVP on the surface of Ag NPs, we have obtained Raman spectra for Ag NPs extracted from aqueous PVP solution after these have been heated for 3 min in air at various temperatures (Fig. 3). Spectral features at  $1613$  and  $1510 \text{ cm}^{-1}$  after heating to  $200 \text{ }^\circ\text{C}$  (Fig. 3(a)) indicate that PVP is still present on the surface of Ag NPs, but peaks at  $1288$ ,  $1350$ , and  $1549 \text{ cm}^{-1}$  show that some PVP has decomposed into  $\alpha\text{-C:H}$ .<sup>19–23</sup> After heating to  $300 \text{ }^\circ\text{C}$  (Fig. 3(b)), residual PVP

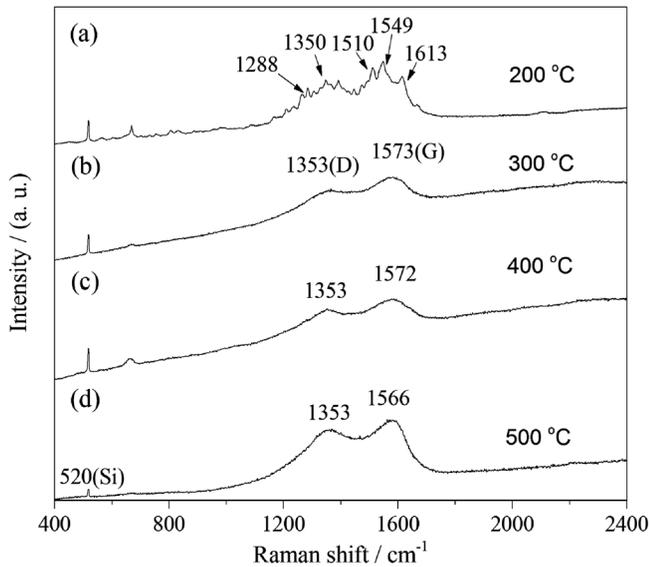


FIG. 3. Raman spectra of Ag NPs heated to different temperatures in air: (a) 200 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C.

is completely converted to  $\alpha$ -C:H. A further increase in heating temperature to 400 and 500 °C converts  $\alpha$ -C:H into  $\alpha$ -C and leads to the appearance of D and G bands at 1353 and 1566  $\text{cm}^{-1}$  (Fig. 3(d)). As expected, the  $I_D/I_G$  ratio increases when the heating temperature increases from 400 to 500 °C. These results indicate that temperatures in excess of  $\sim 200$  °C are required to thermally decompose PVP adsorbed on Ag NPs.

To see if this temperature rise,  $\Delta T$ , is consistent with irradiation conditions,  $\Delta T$  can be estimated from the energy,  $E$ , absorbed during the laser pulse

$$E = 0.25\pi F Q_{abs} X^2 = 0.17\pi\rho C\Delta T X^3, \quad (1)$$

where  $Q_{abs}$  is the particle absorption efficiency,  $F$  ( $\text{J}/\text{m}^2$ ) is the pulse fluence,  $X$  (m) is the equivalent diameter of the nanoparticle,  $\rho$  is the density of Ag =  $1.05 \times 10^4 \text{ kg}/\text{m}^3$ , and  $C = 230 \text{ J}/\text{kg}^\circ\text{C}$  is the heat capacity of Ag. Since  $X \ll \lambda$ ,  $Q_{abs}$  can be calculated using the Rayleigh approximation<sup>27</sup>

$$Q_{abs} = -\left(\frac{4\pi X}{\lambda}\right) I_m \left[\frac{(m^2 - 1)}{(m^2 + 2)}\right], \quad (2)$$

where  $m = n - ik = 0.144 - 5.29i$  is the complex refractive index for Ag<sup>28</sup> at  $\lambda = 800 \text{ nm}$ . Then, taking  $X = 5 \times 10^{-8} \text{ m}$  as a representative size for the Ag NPs in our samples,  $Q_{abs} = 0.0038$ . Fig. 1(c) shows that localized fusion between adjacent Ag NPs can be produced at  $F = 2 \text{ J}/\text{m}^2$  but  $\Delta T$  calculated from Eq. (1) predicts that the temperature rise is  $< 1$  °C under these conditions. This implies that thermal heating is not the causes of the observed decomposition of PVP and welding between Ag NPs at fluences between 200 and 380  $\mu\text{J}/\text{cm}^2$ .

The localization and enhancement of the electric field at the interface between NPs in response to the excitation of plasmon resonances have been identified as an important effect in systems of NPs<sup>29–31</sup> and likely occur under the conditions of the present experiments. Electrons emitted from the surface at these enhanced areas give rise to two primary

effects: the first is to initiate the decomposition of PVP and the conversion of this material to  $\alpha$ -C:H and  $\alpha$ -C, while the second effect will be to produce a softening of the lattice at the Ag surface. Electron impact on the PVP layer surrounding Ag NPs is consistent with the observed decomposition of this material and its conversion to  $\alpha$ -C:H and  $\alpha$ -C<sup>32</sup> and mimics the effects of thermal heating including spallation<sup>33,34</sup> of this layer. It, therefore, appears that modification of the structure of PVP by electron impact is responsible for the similarities between Raman spectra of laser processed and thermally heated material as shown in Figs. 2 and 3.

Because  $\alpha$ -C:H is hydrophobic,<sup>35</sup> Ag NPs coated with this material tend to aggregate to form networks. A reduction in surface energy,<sup>36</sup> as well as dipole-dipole interactions<sup>37</sup> would also favor network formation. After network formation, hotspots arising from plasmon trapping at the interface are generated between adjacent NPs, enhancing the overall emission of electrons and leading to a reduction in volume or elimination of  $\alpha$ -C:H on the surface of NPs. This facilitates welding and the formation of metallic necks between adjacent NPs. It should be pointed out that direct heating of  $\alpha$ -C:H layers can also occur via Ohmic heating induced by the electric field of the incident light wave. At low fluence, electron impact and Ohmic heating effects are minimized, and Ag NPs are connected by  $\alpha$ -C:H bridges (see Figs. 1(a) and 1(b)). Welding of Ag NPs at fluences between 200 and 380  $\mu\text{J}/\text{cm}^2$  is then accompanied by a reduction in the volume of the  $\alpha$ -C:H shells as this is removed by electron impact. It is reasonable to expect that all the  $\alpha$ -C:H bridges can be replaced by welded necks at fluences between 200 and 380  $\mu\text{J}/\text{cm}^2$  if the irradiation time is sufficiently long. The above analyses suggest that the contact geometry between adjacent Ag NPs can be manipulated by controlling the laser fluence.

To evaluate the SPR enhancement effect in samples prepared at different fluence levels, Fig. 4 shows SERS spectra of adenine absorbed on Ag NP deposits after irradiation. In previous studies, it has been shown that the Raman peaks of adenine at 730 and 1327  $\text{cm}^{-1}$  are diagnostic of the SERS enhancement effect.<sup>31,38</sup> Ag NPs joined through highly conjugated carbon chains exhibit a  $10 \times$  larger Raman

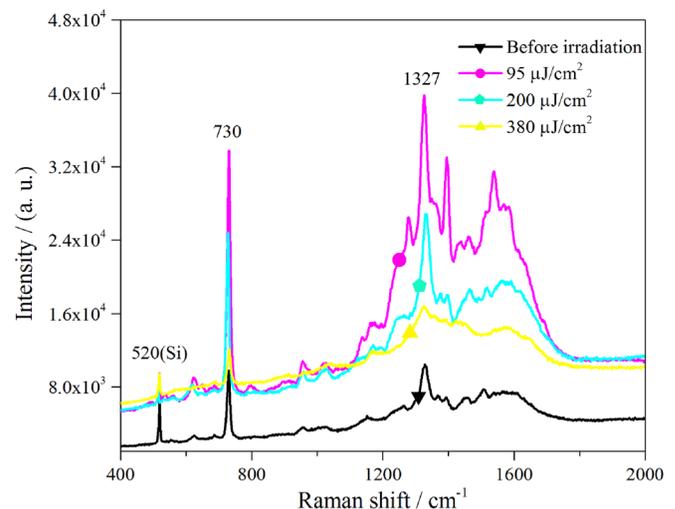


FIG. 4. SERS spectra of adenine solution absorbed on the surface of Ag NPs.

enhancement than single NPs.<sup>39</sup> We have found that the adenine bands are significantly enhanced in SERS spectra of welded Ag NPs relative to samples where joining has not occurred.<sup>31</sup> The spectra in Fig. 4 show that a narrow gap mediated by the presence of an extremely thin  $\alpha$ -C:H film ( $\sim 0.5$  nm thickness) gives even higher SERS enhancement than that occurring in welded NPs. This is consistent with the results of calculations showing that the enhancement cross-section in dimers is largest when the gap between NPs is reduced to 0.4–1 nm and reducing the gap to zero results in a nonlinear reduction of the plasmon-induced field enhancement due to the neutralization of charge density on opposite sides of the gap in response to an induced current flow.<sup>15</sup> The role of the  $\alpha$ -C:H film in producing enhancement of the SERS signal is probably twofold: the first effect is to separate the Ag NPs by a small amount, while a secondary effect may be the facilitation of active adsorption sites at the surface of Ag NPs. It is also worth noting that, in addition to excellent SPR enhancement, the formation of carbon shells on the surface of NPs may inhibit metal-molecule interactions and reduce sensitivity to photochemical damage.<sup>40</sup> As a result, the presence of  $\alpha$ -C:H bridges between Ag NPs, and the fact that the properties of such systems can be tailored through exposure to fs laser pulses, opens up many new possibilities for the application of these materials in nanostructured SERS devices.

#### IV. CONCLUSIONS

In this study, we have found that by adjusting the fs laser pulse fluence during irradiation of PVP coated Ag NPs in aqueous solution, it is feasible to control the separation and bonding within networks of Ag NPs. The primary effect at low fluence ( $\approx 95 \mu\text{J}/\text{cm}^2$ ) is the generation of an  $\alpha$ -C:H coating on individual Ag NPs as a result of the decomposition adsorbed PVP. We show that is the result of electron ejection at hot-spots formed by the trapping of plasmon energy. At higher fluences (typically between 200 and  $380 \mu\text{J}/\text{cm}^2$ ), this effect is large enough to remove some of the  $\alpha$ -C:H layer. Softening of the Ag lattice accompanying electron emission can produce local welding between adjacent Ag NPs. The narrowest gaps between separated Ag NPs ( $< 1$  nm) are found in non-welded samples irradiated at low fluence. A SERS study of Raman spectra of adsorbed adenine indicates that Ag NPs joined by narrow  $\alpha$ -C:H shell possess much higher SPR enhancements than welded or single NPs.

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