



Published in final edited form as:

Nano Lett. 2008 October ; 8(10): 3446–3449. doi:10.1021/nl8023164.

Surface Plasmon-Mediated Energy Transfer in Hetero-Gap Au-Ag Nanowires

Wei Wei, Shuzhou Li, Lidong Qin, Can Xue, Jill E. Millstone, Xiaoyang Xu, George C. Schatz*, and Chad A. Mirkin*

Department of Chemistry and International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113 USA

Abstract

We report the observation of energy transfer from a gold (Au) nanodisk pair to a silver (Ag) nanowire across a 120 nm gap via surface plasmon resonance (SPR) excitation. The enhanced electromagnetic (EM) fields generated by Au SPR excitation induce oscillation of the conduction electrons in the Ag segment, transferring energy to it even though the Ag segment has only weak resonant interactions with the incident electromagnetic radiation. The induced Ag SPR produces strong EM fields at the position of the Ag segment, leading to a Raman signal ~15 times greater than when the Ag segment is alone (not adjacent to the Au nanodisk pair). The Raman intensity is found to depend nonlinearly on the incident laser intensity for laser power densities of 10 kW/cm², which is consistent with the results of electromagnetic theory calculations which are not able to account for the factor of 15 enhancement based on a linear mechanism. This suggests that energy transfer from the Au disk pair to the Ag segment involves an enhanced nonlinear polarization mechanism such as can be produced by the electronic Kerr effect or stimulated Raman scattering.

Metallic nanomaterials with localized surface plasmon resonances (SPRs) have been extensively studied for their use in chemical and biological detection systems,¹⁻⁷ photocatalysis,⁸ and solar energy conversion.⁹ When the localized SPRs of nanomaterials are excited, enhanced electromagnetic (EM) fields at the surface of the nanostructure are generated. These fields can be several orders of magnitude larger than the incident optical excitation field.^{10, 11}

These enhanced fields have been used to achieve SP-mediated energy transfer with nanostructures.^{10,12-14} However, investigations thus far have been limited to structures made of a single composition. Indeed, the study of energy transfer between different nanomaterials via SPR is rare,^{15, 16} despite the fact that such studies could provide significant fundamental insight and lead to highly functional architectures. Here, we report a system comprised of a gold (Au) nanodisk pair separated from a silver (Ag) segment by a nanometer scale gap that is capable of efficiently interacting with red light at the Au end and transferring this energy to the Ag segment, leading to Raman emission from molecules on the Ag segment. We show that this leads to significant enhancement in Raman intensities compared to the case where the Ag segment is irradiated in the absence of the Au, and we also find a nonlinear power dependence that is suggestive of important contributions from nonlinear susceptibility on the Au nanodisk pair. A theoretical analysis is provided which establishes the linear and nonlinear components of the scattering process.

*chadnano@northwestern.edu; schatz@chem.northwestern.edu .

Supporting Information Available: Full descriptions of materials and methods are available free of charge via the Internet at <http://pubs.acs.org>.

Exploring energy transfer between different metallic materials on the nanoscale is interesting from both scientific and technological standpoints. Such studies will lead to a more comprehensive understanding of energy transfer mechanisms and open the door to expand the applications of metal-based SPRs. The ideal nanostructures for this study consist of two different metallic materials on opposite sides of a well-defined nanoscale gap, with the SPR mode of one material in resonance with the incident radiation, and the SPR of the other material out of resonance (although having “dark” plasmon modes that can be excited with near-field excitation from the resonantly excited material). To facilitate this study, one needs an efficient tool for fabricating the above-mentioned multisegmented nanostructures. Specifically, one needs control over nanostructure dimension, distance, and orientation. Among the available nanofabrication approaches,^{17, 18} On-Wire Lithography (OWL) is a particularly powerful method for achieving this level of control because of its reliability, resolution, flexibility, and throughput.¹⁹ OWL can be used to make many types of metal nanostructures with dimensions that can be controlled from 2.5 nm to many μm .^{19, 20} More importantly, one can use OWL to fabricate nanostructures made of different materials on opposite sides of a nanoscale gap. In principle, this technique can be used to synthesize any electrochemically platable metal with plasmon modes that are suitable for energy transfer.

In this letter, we use OWL, a template synthesis method,^{21, 22} to fabricate Au-Ag multisegmented nanowires with well-defined gaps between different segments. We employ surface enhanced Raman scattering (SERS) (a spectroscopic phenomenon based on SPR^{2, 3, 5, 6, 23, 24}) to investigate the locally enhanced EM fields on the nanowires, and their ability to induce energy transfer across the multisegmented metallic nanostructures. Importantly, our results demonstrate that energy can be efficiently transferred from an Au nanodisk pair to an Ag segment over at least a 120 nm gap through SPR excitation.

In a typical experiment, a 360 nm diameter nanowire, which contains a pair of 120 ± 18 nm long Au nanodisks that are separated by a 30 ± 8 nm gap (termed as Au nanodisk pair) and one Ag segment that is separated by a 120 ± 15 nm gap from the Au nanodisk pair (Figure 1a, upper left), was prepared. The 120 nm Au nanodisk thickness and 30 nm gap distance were chosen based upon previous results from our group,²⁵ which demonstrated that for this nanodisk architecture, a structure with these dimensions exhibits the largest SERS enhancement. To this basic structure, we added Au and Ag segments with a 120 nm gap, which were physically separated from the initial gap structures by 1 μm (Figure 1a, lower right). The 120 nm gap between the Au nanodisk pair and the Ag segment was deliberately chosen to be relatively large in order to eliminate hybridization of the Ag and Au plasmon resonances and the possibility of having accidental overlap with the excitation wavelength. This distance also allows one to spatially address and determine which segment is responsible for the Raman scattering measured by confocal Raman spectroscopy. These structures were modified with a SERS probe, p-mercaptobenzoic acid (pMA), prior to characterization by Raman spectroscopy (see Supplementary Information).

The largest SERS signal is observed from the Ag segment end that is separated 120 nm from the Au nanodisk pair (point A, Figure 1c). In the scanning Raman image, the most intense SERS signal is from the area that includes the Au nanodisk pair and Ag segment. The three-dimensional band that represents a quantification of the Raman scattering in this region is not symmetrical. Instead, this band contains a shoulder that is always found on the left side and can be seen more clearly in the line plot of Raman scattering intensity along the long axis of the nanofabricated wire (Figure 1e). This shoulder is assigned to the Au nanodisk pair while the more intense band is assigned to the long Ag segment end that is 120 nm from the Au nanodisk pair. To confirm this assignment, we prepared another multisegmented nanowire structure (Figure 1b), in which an individual Au nanodisk pair (far left, Figure 1b) was added as a reference for the Au nanodisk pair-Ag segment structure. With this structure,

one can study the SERS response of the Au nanodisk pair separate from the response of the Au nanodisk pair-Ag structure, which exhibits an intense band and contains a shoulder. In the scanning Raman image of this structure (Figure 1d), one can clearly see that the response from the individual Au nanodisk pair (point A, Figure 1d) is the cause of the shoulder in the Au nanodisk pair-Ag segment structure (point B, Figure 1d), given that the two intensities are almost identical (dotted line, Figure 1f). The above observations show that the maximum enhancement is observed from the Ag segment end that is 120 nm from the Au nanodisk pair. Furthermore, if one compares the response from the Ag segment end adjacent to the Au nanodisk pair (point A, Figure 1c) to the response from the other end that is not adjacent to this nanostructure (point B, Figure 1c), the SERS intensity is approximately 15 times larger (compare the intensity at point A and point B in Figure 1c). In other words, the SERS signal from the Ag segment in the presence of the near-field of the Au nanodisk pair is 15 times larger than is obtained from the Ag segment alone.

It has been shown that the SERS intensity directly correlates with the strength of the locally enhanced EM fields that are generated by exciting the localized SPR on the surfaces of these nanostructures.²³⁻²⁵ To have efficient excitation of a localized SPR, the photon energy of incident radiation must be in resonance with the SPR mode, which can be easily determined from the extinction spectrum of the nanostructure. The dark field extinction spectrum of the separated Au nanodisk pair shows SPR modes at λ_{max} approximately equal to 550 and 640 nm (Figure 2a, black line); for the Ag segment λ_{max} is approximately equal to 450 nm (Figure 2a, red line). When the Au nanodisk pair is brought into proximity with the Ag segment (separated by 120 nm), the extinction spectrum simply appears as a superposition of the two spectra above. These results correlate very well with theoretical calculations using the discrete dipole approximation (DDA) method (Figure 2b). This observation indicates that the nearby Au nanodisk pair does not change the absorption/scattering properties of the Ag segment (i.e., plasmon hybridization effects are weak) and suggests that the Ag segment only has a weak SPR response at the 632.8 nm laser wavelength that was used for the SERS experiments. These results are consistent with the weak SERS signals observed from the ends of the Ag segments that are not associated with an adjacent Au segment in the Raman images (point B and E, Figure 1c).

To provide more evidence for the above conclusions, a nanowire structure containing a Pt segment and an Ag segment with a 120 nm gap was designed (inset of Figure S2a). The SPR modes of Pt are in the UV region of the spectrum and are not in resonance with a 632.8 nm laser.²⁶ If one assumes that the intense SERS signals were simply from the Ag segment itself, then it should not matter whether the nearby segment is Au or Pt, and the Pt-Ag junction should display an intense SERS signal similar to the signal observed from the Au-Ag junction. However, this Pt-Ag nanostructure did not exhibit a significant SERS signal under identical experimental conditions (Figure S2b).

From the experiments described thus far, one can conclude that the strong SERS signal is not from the direct SPR excitation of the Ag segment by the 632.8 nm laser, making energy transfer the primary candidate to describe the above observations. The disappearance of the strong SERS signal, once the Au nanodisk pair is replaced with a Pt segment, is also consistent with the hypothesis that the energy must be transferred from the Au nanodisk pair to the Ag segment to excite its SPR, resulting in a large Raman signal.

In order to explore the origin of the energy transfer from the Au nanodisk pair to the Ag segment, the correlation between laser power and Raman intensity was investigated. Interestingly, the SERS signal from the Ag segment end that is 120 nm spaced from the Au nanodisk pair (main peak, point A, Figure 1c) increases nonlinearly (quadratically) with laser power (Figure 3) for powers of $\sim 10 \text{ kW/cm}^2$. A similar quadratic power dependence

also was observed from the individual Au nanodisk pair (Figure S4). However, for the Ag alone (not associated with Au nanodisk pair), the SERS intensity increases linearly with the laser power (Figure S5). The above results are in agreement with electromagnetic theory calculations (see Supplementary Information), which show that a linear process alone can only account for a factor of less than 4 of the observed factor of 15 enhancement in the SERS intensity due to coupling between the Au nanodisk pair and Ag segment.

There have been many suggestions in the past that the strong nano-localized EM fields associated with SPR excitation can induce enhanced nonlinear-optical phenomena.^{23, 27} Indeed there is ample precedent for multiple plasmon excitation effects for Au and Ag nanostructures,²⁸⁻³⁰ including photoemission yields that are enhanced by up to 2 orders of magnitude.²⁸ In addition, some researchers³⁰ have suggested that when the excitation wavelength matches the SPR, multiple plasmon resonance excitations can occur even with weak radiation (rather than an intense laser) leading to enhanced photoluminescence. However the consequences of nonlinear excitation for SERS measurements have rarely been reported.

Baltog *et al.*³¹ reported stimulated Raman scattering threshold of 40 mW for copper phthalocyanine on Ag gratings and 515 nm irradiation, corresponding to a power density threshold of 30 kW/cm². They interpreted their results in terms of excitation of propagating plasmons on the grating surface. It is not clear how this mechanism would apply in the present case, but stimulated Raman scattering (as 4-photon process) is one mechanism by which the present results can be understood, and the power threshold in the Baltog experiments is not far from what we find. However one problem with this mechanism is that the nonlinear process is associated with the molecules on the Ag segment, and this is where the field is likely to be weak due to the large gap between the strongly excited Au nanodisk pair and the Ag segment.

Another possibility (also involving 4-photons) is for the a mechanism that that we might term “Kerr-enhanced SERS”, in which the induced dipole at the Au nanodisk pair is enhanced above that obtained from linear electrodynamics (i.e., the first order susceptibility) as a result of a third-order nonlinear response (electronic Kerr effect). This nonlinear induced polarization mechanism is related to recently reported SPR-enhanced optical Kerr results for Au and Cu nanoparticles.^{32, 33} For Au nanoparticles at 532 nm, it was found that powers in the 1-2 MW/cm² range were required to produce significant results, corresponding to the nonlinear susceptibilities of $\chi^{(3)} = \sim 5 \times 10^{-8}$. Other estimates of $\chi^{(3)}$ have provided larger values (10^{-7} ³⁴, 5×10^{-6} ³⁵) so there is some uncertainty in these results. The $\chi^{(3)}$ values decrease with increasing particle size, but in the present case surface roughness in the gold disks²⁵ would make the effective particle size much smaller than the dimensions of the disks. The conditions of the Kerr experiments were such that only weak plasmon resonance enhancements (factor of 5-10) of the Kerr susceptibility were found. In the present application, the classical electrodynamics calculations indicate that a plasmon ($|E|^4$) enhancement contribution to the Kerr susceptibility of at least 10^3 is possible. If we use the Ryasnyanskiy *et al.*³³ estimates of power density and $\chi^{(3)}$, then the 10^2 larger field enhancement would drop the threshold for Kerr enhancement to the 10 kW/cm² power that we have used. Obviously further work is needed to verify whether the Kerr or stimulated Raman mechanisms is to be preferred.

In conclusion, OWL can be used to fabricate multimetallic structures capable of efficiently transferring energy across a 120 nm gap. Upon SPR excitation of an Au nanodisk pair, energy is transferred to an Ag segment by inducing the oscillation of the Ag conduction electrons, despite the fact that the Ag SPR is only weakly excited by the 632.8 nm laser. Importantly, this energy transfer process involves multiple SPR excitations of the Au

nanodisk pair through a 4-photon mechanism, leading SERS on the Ag segment that is enhanced by a factor of 15 compared to the Ag segment in the absence of the Au nanodisk pair.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported in part by the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Award Number EEC-0647560. Any opinions, findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect those of the National Science Foundation. C.A.M. acknowledges the Office of Naval Research (ONR) and the NSSEF program of the DoD for generous financial support. C.A.M is grateful for a NIH Director's Pioneer Award. G. C. S and S. L. thank the U.S. Department of Energy under grant No. DEFG02-03-ER15487.

References

1. Alivisatos P. *Nat. Biotech.* 2004; 22:47–52.
2. Graham D, Faulds K. *Chem. Soc. Rev.* 2008; 37:1042–1051. [PubMed: 18443688]
3. Nie SM, Emory SR. *Science.* 1997; 275:1102–1106. [PubMed: 9027306]
4. Eustis S, El-Sayed M. J. *Phys. Chem. B.* 2005; 109:16350–16356. [PubMed: 16853078]
5. Keating CD, Kovalski KM, Natan MJ. *J. Phys. Chem. B.* 1998; 102:9404–9413.
6. Jiang J, Bosnick K, Maillard M, Brus L. *J. Phys. Chem. B.* 2003; 107:9964–9972.
7. Murphy CJ, Gole AM, Hunyadi SE, Stone JW, Sisco PN, Alkilany A, Kinard BE, Hankins P. *Chem. Commun.* 2008:544–557.
8. Watanabe K, Menzel D, Nilius N, Freund H-J. *Chem. Rev.* 2006; 106:4301–4320. [PubMed: 17031988]
9. Westphalen M, Kreibig U, Rostalski J, Luth H, Meissner D. *Sol. Energy Mater. Sol. Cells.* 2000; 61:97–105.
10. Krenn JR. *Nat. Mater.* 2003; 2:210–211. [PubMed: 12690387]
11. Aizpurua J, Garnett WB, Lee JR, Abajo F. J. G. d. Brian KK, Mallouk T. *Phys. Rev. B.* 2005; 71:235420.
12. Andrew P, Barnes WL. *Science.* 2004; 306:1002–1005. [PubMed: 15528438]
13. Maier SA, Kik1 PG, Atwater HA, Meltzer S, Harel E, Koel BE, Requicha AAG. *Nat. Mater.* 2003; 2:229–232. [PubMed: 12690394]
14. Ozbay E. *Science.* 2006; 311:189–193. [PubMed: 16410515]
15. Dickson RM, Lyon LA. *J. Phys. Chem. B.* 2000; 104:6095–6098.
16. Kalsin AM, Paszewski M, Pinchuk AO, Schatz GC, Grzybowski BA. *Nano Lett.* 2006; 6:1896–1903. [PubMed: 16967998]
17. Menke EJ, Thompson MA, Xiang C, Yang LC, Penner RM. *Nat. Mater.* 2006; 5:914–919. [PubMed: 17057701]
18. Xia Y, Rogers JA, Paul KE, Whitesides GM. *Chem. Rev.* 1999; 99:1823–1848. [PubMed: 11849012]
19. Qin L, Park S, Huang L, Mirkin CA. *Science.* 2005; 309:113–115. [PubMed: 15994551]
20. Qin L, Jang J-W, Huang L, Mirkin CA. *Small.* 2007; 3:86–90. [PubMed: 17294475]
21. Martin CR. *Science.* 1994; 266:1961–1966. [PubMed: 17836514]
22. Preston CK, Moskovits M. *J. Phys. Chem.* 1993; 97:8495–8503.
23. Moskovits M. *Rev. Mod. Phys.* 1985; 57:783–826.
24. Hornyak GL, Patrissi CJ, Martin CR. *Nanostruct. Mater.* 1997; 9:705–708.
25. Qin L, Zou S, Xue C, Atkinson A, Schatz GC, Mirkin CA. *Proc. Natl. Acad. Sci. U.S.A.* 2006; 103:13300–13303. [PubMed: 16938832]

26. Ren B, Liu G-K, Lian X-B, Yang Z-L, Tian Z-Q. *Anal. Bioanal. Chem.* 2007; 388:29–45. [PubMed: 17318524]
27. Stockman MI. *Phys. Rev. Lett.* 2004; 93:137404. [PubMed: 15524758]
28. Lehmann J, Merschdorf M, Pfeiffer W, Thon A, Voll S, Gerber G. *Phys. Rev. Lett.* 2000; 85:2921. [PubMed: 11005968]
29. Kennerknecht C, Hovel H, Merschdorf M, Voll S, Pfeiffer W. *Appl. Phys. B.* 2001; 73:425–429.
30. Lin HY, Chen YF. *Appl. Phys. Lett.* 2006; 88:101914.
31. Baltog I, Primeau N, Reinish R, Coutaz JL. *J. Opt. Soc. Am. B.* 1996; 13:656.
32. Karthikeyan B, Anija M, Suchand Sandeep CS, Muhammad Nadeer TM, Philip R. *Opt. Commun.* 2008; 281:2933–2937.
33. Ryasnyanskiy AI, Palpant B, Debrus S, Pal U, Stepanov A. *J. Lumin.* 2007; 127:181–185.
34. Xenogiannopoulou E, Iliopoulos K, Couris S, Karakouz T, Vaskevich A, Rubinstein I. *Adv. Funct. Mater.* 2008; 18:1281–1289.
35. Liao HB, Wen W, Wong GKL. *J. Appl. Phys.* 2003:93.

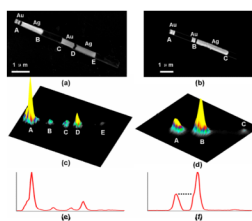


Figure 1.

Scanning electron microscopy and confocal Raman microscopy images of multisegmented nanowires. (a) Left to right: a pair of 120 ± 18 nm long Au nanodisks (360 nm diameter) with a 30 ± 8 nm gap and separated from a $1.2 \mu\text{m}$ Ag segment by a 120 ± 15 nm gap. These structures are separated from a second set of nanostructures in the wire by a $1 \mu\text{m}$ gap. The second set of nanostructures in the wire consists of a 600 nm long Au segment separated by a 120 ± 15 nm gap from a $1 \mu\text{m}$ Ag segment. (b) Left to right: a pair of 120 ± 18 nm long Au nanodisks (360 nm diameter) with a 30 ± 8 nm gap separated from a second set of nanostructures by $1.5 \mu\text{m}$. The second set of nanostructures consist of a nearly identical Au nanodisk pair separated by 120 ± 15 nm from a $3 \mu\text{m}$ Ag. (c) and (d) are the corresponding confocal Raman microscopy images for the nanowires in (a) and (b) functionalized with pMA. The Raman signal intensities in (c) and (d) are not normalized and can not be directly compared. (e) and (f) are Raman scattering intensity line plots along the long axis of the multisegmented nanowires taken from the images displayed in (c) and (d), respectively.

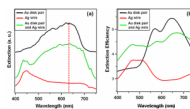


Figure 2.

(a) Dark field extinction spectra of an individual Au nanodisk pair (black), an Ag nanowire (red) and a multisegmented nanowire that contains an Au nanodisk pair and an Ag nanowire (green). The spectra were taken on the wires described in Figure 1. The red dotted line indicates the wavelength of the laser (632.8 nm) used in the Raman spectrum measurements.

(b) Extinction coefficient for the three structures in (a) calculated by the discrete dipole approximation (DDA) method.

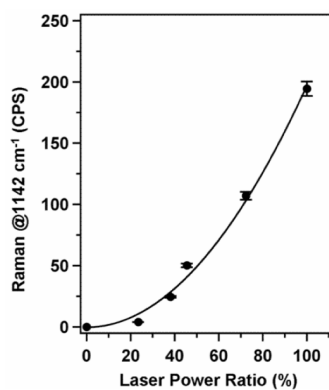


Figure 3. Raman scattering from the Ag segment end that is separated by 120 nm from the Au nanodisk pair as a function of excitation laser power. Note that the abscissa label is “laser power ratio” referring to the highest power used in the SERS measurement. Data fitting analysis indicates a quadratic dependence of SERS intensity on the excitation power.