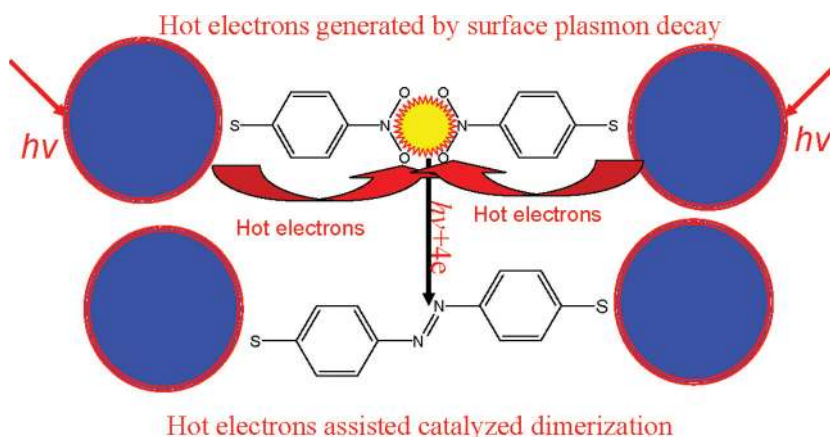# A Novel Application of Plasmonics: Plasmon-Driven Surface-Catalyzed Reactions

Mengtao Sun* and Hongxing Xu

Hot electrons generated by surface plasmon decay

Hot electrons

Hot electrons assisted catalyzed dimerization

From the Contents

The first experimental and theoretical evidence of the surface-catalyzed reaction of p,p′-dimercaptoazobenzene (DMAB) produced from para-aminothiophenol (PATP) by local surface plasmons was reported in 2010, and since that time a series of investigations have supported these findings using different experimental and theoretical methods. Recent work has also found that local plasmons can drive a surface-catalyzed reaction of DMAB converted from 4-nitrobenzenethiol (4NBT), assisted by local surface plasmons. There are at least three important discoveries in these investigations: 1) in the field of surface-enhanced Raman scattering (SERS) the widely accepted misinterpretation (since 1994) that the chemical mechanism resulting in three additional Raman peaks of PATP in Ag or Au solutions has been corrected with a new mechanism; 2) it is confirmed that SERS is not always a noninvasive technique, and under certain conditions cannot always obtain the vibrational fingerprint information of the original surface species; 3) a novel method to synthesize new molecules, induced by local surface plasmons or plasmon waveguides on the nanoscale, has been found. This Review considers recent novel applications of plasmonics to chemical reactions, especially to plasmon-driven surface-catalyzed reactions.

1. Introduction

Surface plasmons (SPs) are collective electron oscillations confined evanescently along the interface between a conductor and a dielectric.[1] When a SP couples with a photon, the resulting hybridised excitation is called a surface plasmon polariton (SPP). This SPP can propagate along the surface of a metal until the energy is lost either via absorption in the metal, or radiation into free space.[2] The local SPs and propagating SPPs have been widely applied in surface plasmon resonance sensors,[2,3] surface-enhanced Raman scattering (SERS),[4] quantum communication,[5] super-resolution microscopy,[6] metamaterials,[7,8] plasmonic circuitry for next generation IT,[9–11] cloaking,[12] photothermal cancer therapy,[13] holography[14] etc. Recently, the novel application of plasmonics on chemical reactions have been widely investigated,[15–44] such as photochromic reactions,[15] polymerization,[16,17] photochemical isomerization,[18] photodissociation,[19] and photocatalytic reactions.[20–42] In this review, we focus mainly on the application of plasmonics to surface-catalyzed reactions assisted by local SPs and propagating surface plasmons, which were revealed by SERS spectroscopy.

Since its discovery SERS[45,46] has been studied extensively, both experimentally and theoretically[4,47–55] because of its extremely high surface sensitivity and powerful application on fingerprint vibrational spectroscopy in qualitative and quantitative analysis, even at the single-molecule level. There is general agreement that SERS occurs by electromagnetic enhancement (EM) and chemical enhancement (charge transfer) mechanisms. The former is caused by local SPPs,[4,47–49] which usually enhance the Raman spectrum over a large frequency range, and the latter is due to changes in the electronic structure of molecules adsorbed on metal surfaces, whereby some Raman peaks undergo enormous selective enhancement.[50–55]

Extensive experimental studies have been done on SERS of 4-aminothiophenol (PATP, see **Figure 1**a) adsorbed on different metal surfaces, and in the junction of metal-molecule-metal systems.[20–29,56–79] The enhancement mechanism for three strongly enhanced Raman peaks at 1143, 1390, and 1432 cm^{-1} was first interpreted as a chemical mechanism by Osawa in 1994.[57] Since then, many papers have been published, and these three strongly enhanced Raman peaks were widely considered as experimental evidence for a chemical mechanism of SERS.[57–71,76–80] However, such experimental SERS spectra of PATP have not been convincingly reproduced by simulations untill 2009. In 2010, Wu and co-workers predicted theoretically

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that p,p'-dimercaptoazobenzene (DMAB, see Figure 1b) can be produced from PATP by a catalytic coupling reaction on silver nanoparticles;[23] and the calculated Raman spectra of DMAB agree well with those experimental SERS spectra from PATP.

Using experimental time-dependent SERS spectra, we provided experimental and theoretical evidence on the surface-catalyzed reaction of DMAB produced from PATP, assisted by local SPs in 2010.[20] Since then, a series of investigations have been reported to support, or further confirm the conclusions above using different experimental and theoretical methods.[21,22,24–31] We also confirmed that DMAB can be produced from 4-nitrobenzenethiol (4NBT, see Figure 1(c)),[32] and furthermore, we also investigated substrate-, wavelength-, and time-dependent plasmon-assisted surface-catalyzed reactions of 4NBT dimerizing to DMAB on Au, Ag, and Cu films.[33]

In this review, we will firstly introduce why, when, and how the issue of surface-catalyzed reaction assisted by SPs was proposed; secondly, we will summarize the recent progress in this issue; thirdly conclusions are drawn, and lastly this presentation is closed with the future outlooks.

2. Plasmon-Driven Surface-Catalyzed Reaction

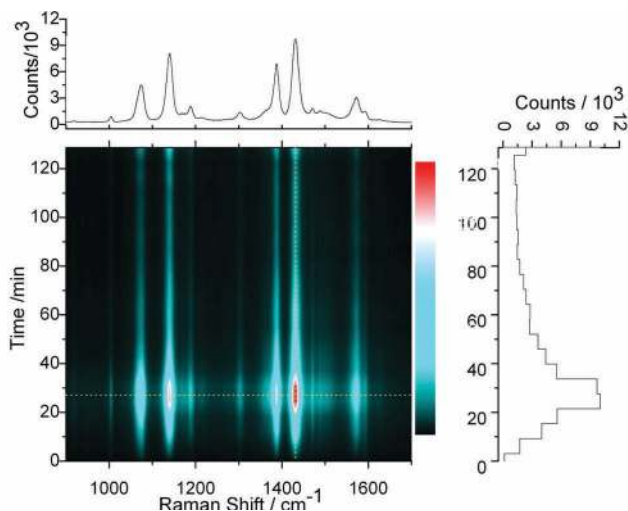### 2.1. Is SERS Always a Noninvasive Technique?

PATP is an increasingly important molecule for use as a probe in SERS, because of its strong interaction with Ag
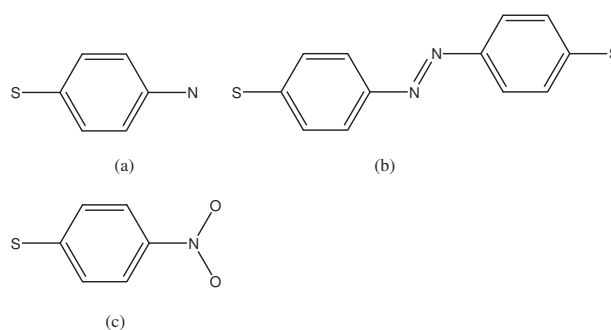
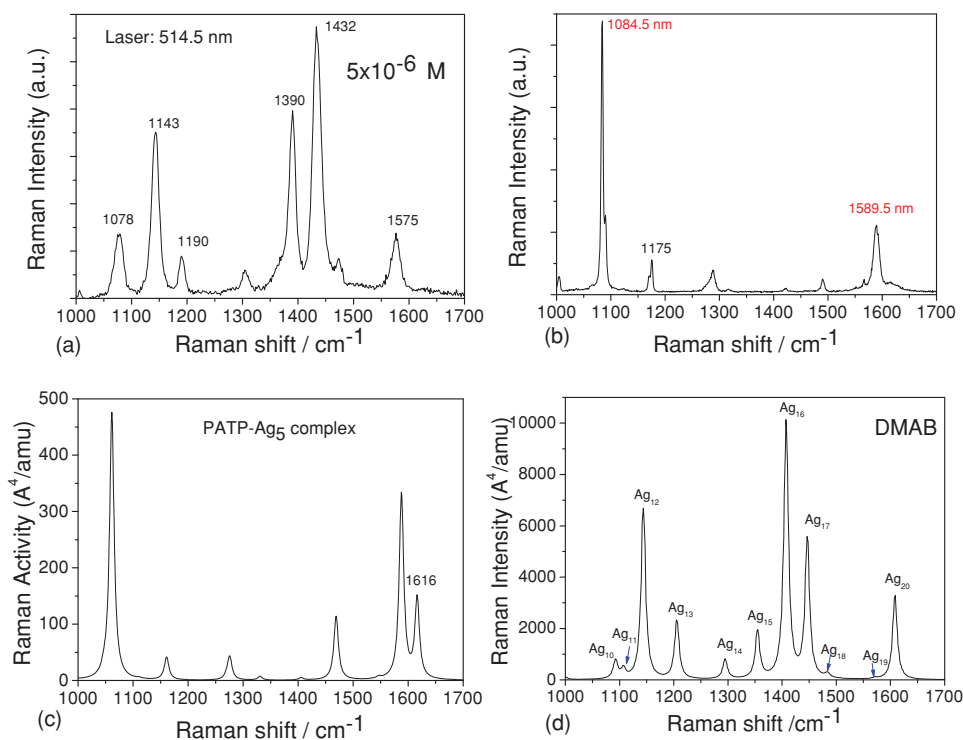**Figure 1.** Chemical structures of: a) PATP, b) DMAB, and c) 4NBT.

Figure 2. The time-dependent SERS of DMAB produced from PATP at a molecular concentration of 10^{-5}. Reproduced with permission.[20] Copyright 2010, American Chemical Society.

attributed to another molecule, namely an azobenzene which can be formed on silver films from PATP.[85,86] Recent work reported by Wu and coworkers predicted theoretically that the 'b$_2$ modes' of PATP can in fact be assigned to a new compound, namely DMAB, produced by a catalytic coupling reaction of PATP on silver nanoparticles.[23] These predictions are a great challenge to SERS, because SERS has long been considered as a noninvasive technique that can obtain the fingerprint vibrational information of surface species. Since 2010, a series of experimental and theoretical investigations have been reported to support, or further confirm the above conclusions that DMAB can be produced from PATP by local SPPs and propagating surface plasmons,[20–22,24–31] Although there are still a few works arguing that in 2011.[77–80]

2.2. Surface-Catalyzed Reaction of DMAB Produced from PATP by SPs

Using experimental time-dependent SERS spectra (see **Figure 2**(a)), in combination with theoretical calculations, we showed convincing evidence of the surface-catalyzed reaction of DMAB produced from PATP by local SPs in 2010.[20] Comparing SERS spectra of PATP in Ag sol (**Figure 3**(a)) with normal Raman spectroscopy of PATP (see Figure 3(b)), it is found that there are three additional Raman peaks 1143, 1390, and 1432 cm^{-1}. These three additional strongly enhanced Raman peaks were considered as the experimental evidence for a chemical enhancement mechanism.[57] The simulated SERS spectroscopy of PATP adsorbed on Ag$_5$ clusters (see Figure 3(c)) can unfortunately not be reproduced very well.

and Au, the intense SERS signal, and the significance in molecular electronics.[57,81–84] Ever since Osawa et al.[57] reported potential- and wavelength-dependent SERS spectra of PATP on silver electrodes, it has been regarded as a model adsorbate for probing the chemical enhancement mechanism in SERS, where several additional lines are identified and attributed to b$_2$ symmetry. While, Fujishima and coworkers were the first to mention that the recorded Raman peaks assigned to p-ATP could be equally
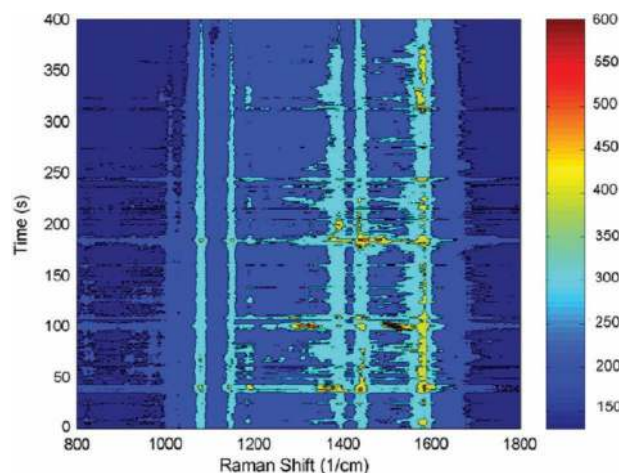

Figure 3. a) Experimental SERS spectra of DMAB excited at 514.5 nm, b) the experimental normal Raman spectrum of PATP, c) theoretical SERS spectrum of a PATP–Ag$_5$ complex, and d) simulated Raman spectrum of DMAB. Reproduced with permission.[20] Copyright 2010, American Chemical Society.

Table 1. Vibrational modes of DMAB with symmetry in the region from 1000 cm^{-1} to 1650 cm^{-1}, and Raman activity (A^4/amu) (in the parenthesis). Data reprinted with permission.[20] Copyright 2010, American Chemical Society.

Bu$_{10}$: 1090.9 (0)	Ag$_{10}$:1091.7 (721.0)
Ag$_{11}$: 1106.3 (359.9)	Bu$_{11}$: 1109.4 (0)
Ag$_{12}$:1143.2 (6656.6)	Bu$_{12}$: 1153.6 (0)
Ag$_{13}$:1205.1 (2291.5)	Bu$_{13}$: 1255.9 (0)
Bu$_{14}$: 1290.5 (0)	Ag$_{14}$:1294.4 (777.0)
Bu$_{15}$: 1350.0 (0)	Ag$_{15}$:1354.4 (1858.7)
Ag$_{16}$:1407.2 (10098.9)	Bu$_{16}$: 1428.6 (0)
Ag$_{17}$:1446.5 (5432.9)	
Ag$_{18}$:1483.6(173.6)	Bu$_{17}$: 1485.4 (0)
Bu$_{18}$: 1565.9 (0)	Ag$_{19}$:1571.6 (46.4)
Bu$_{19}$:1606.1(0)	Ag$_{20}$:1608.5 (3292.6)

Figure 5. Waterfall plot of a time-series of p-ATP SERS spectra. Reproduced with permission.[24] Copyright 2010, Elsevier.

According to our assumption that PATP is dimerized to DMAB by a surface-catalyzed reaction, we simulated the Raman spectrum of DMAB (see Figure 3(d)). It is surprising that Raman spectroscopy of DMAB is perfectly reproduced in the SERS spectroscopy of PATP in Ag sol.[20] All of the strongly enhanced Raman peaks of DMAB are symmetric a$_g$ vibrational modes, and they are direct evidence for the formation of DMAB from PATP via the –N=N– bond, and assigned as a$_{g12}$, a$_{g16}$ and a$_{g17}$ symmetric vibrational modes. Furthermore, the asymmetric b$_u$ vibrational modes, without Raman intensity in the measurements, which accompany those symmetric a$_g$ modes, are also assigned (see **Table 1**). These have also been used to assign the HV-TERS in Ref.[22].

The surface-catalyzed reaction of DMAB produced from PATP were experimentally confirmed by surface mass spectrometry (SMS), SERS, and electrochemistry of the synthesized DMAB, which are consistent well with theoretical calculations.[21] The SMS measurement[21] was made over the PATP-adsorbed Ag electrode after having been illuminated with a high-power laser. PATP-adsorbed and blank roughened Ag electrodes were used as controls. The molecular ion peaks at *m/z* of 245.5
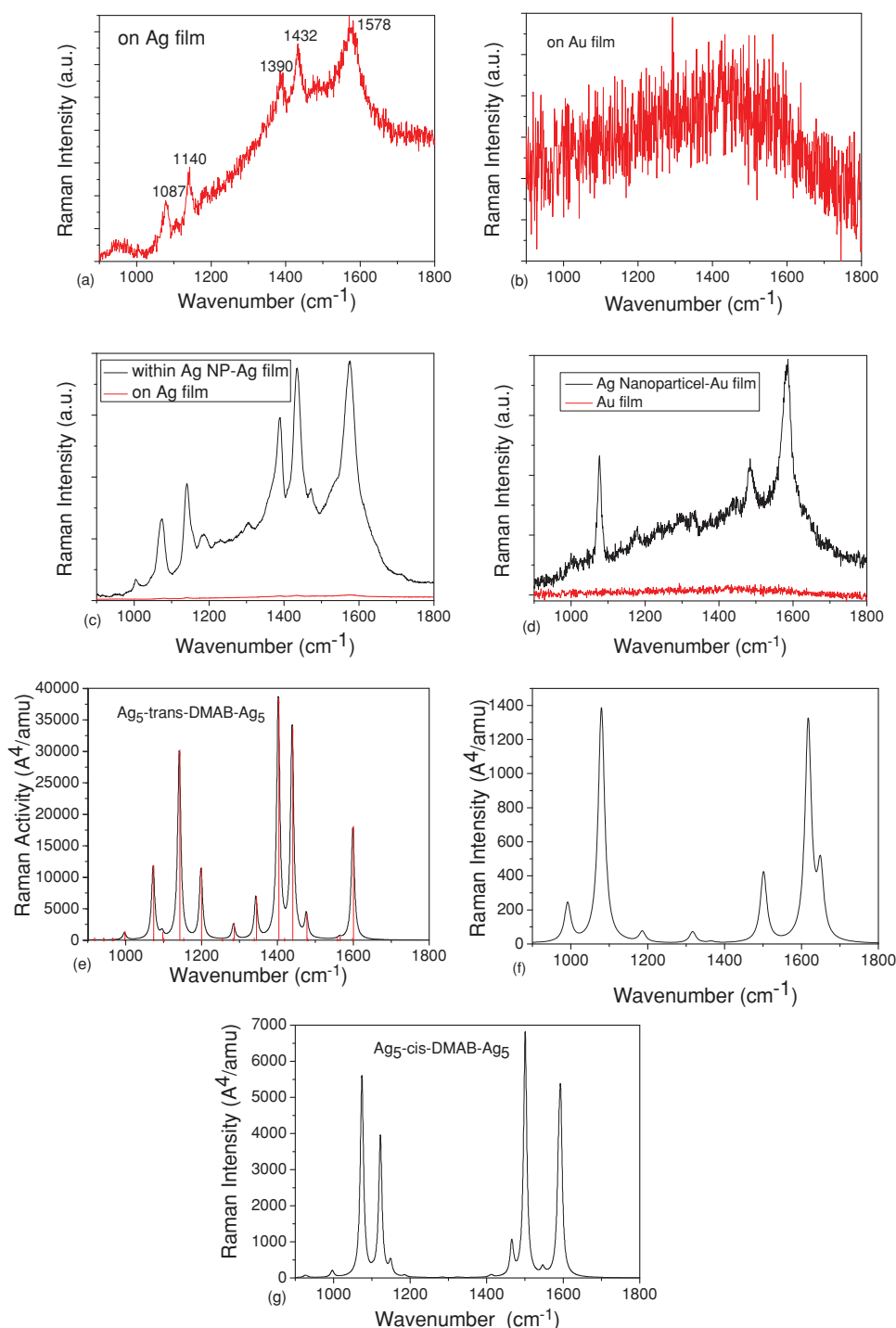
and 164 can be assigned to "H+S–Ph–N=N–Ph–S" fragment (**Figure 4**a(i)) and "K+S–Ph–NH$_2$", respectively. The 245.5 *m/z* peak in Figure 4a (ii and iii) serving as a control was not observed. SMS strongly demonstrated the formation of DMAB from PATP under the illumination of the high-power laser. Furthermore, DMAB (that is commercially unavailable) was synthesized successfully, and the SERS profiles of DMAB were measured (see Figure 4b). It was found that these two spectra had essentially identical spectral features, which revealed that they are from the same species.

Also in 2010, new evidence for the production of DMAB by a catalytic coupling reaction of PATP on metallic nanostructures was provided experimentally. Canpean et al.[24] successfully exploited time-dependent SERS measurements (see **Figure 5**) to distinguish between PATP and DMAB (produced by a catalytic coupling reaction of p-ATP on polystyrene spheres decorated with gold nanoparticles). The calculated auto-correlation functions for the time-dependent intensity fluctuations of the recorded SERS bands showed that the a$_1$ modes of PATP at 1081 and 1584 cm^{-1} and the a$_g$ modes of DMAB at 1147, 1395, and 1440 cm^{-1} respectively, exhibit different decay behavior, which supports the idea of the co-existence of both molecular species.

Furthermore, experimental and theoretical results (see **Figure 6**) revealed that the DMAB can be produced in the junction between (Ag nanoparticle)–molecule–Ag film, while it cannot be produced in the junction between (Ag nanoparticle)–molecule–Au film.[26] We also confirmed that the produced DMAB should be *trans*-DMAB, not *cis*-DMAB.[26] While in Au and Cu solutions, the DMAB can be produced from PATP by a surface-catalyzed reaction, as supported by theoretical calculations (see **Figure 7**).[27] These experimental results are strongly supported by Wu's theoretical work.[25] Our experimental results[26,27] and Wu's calculations[25]
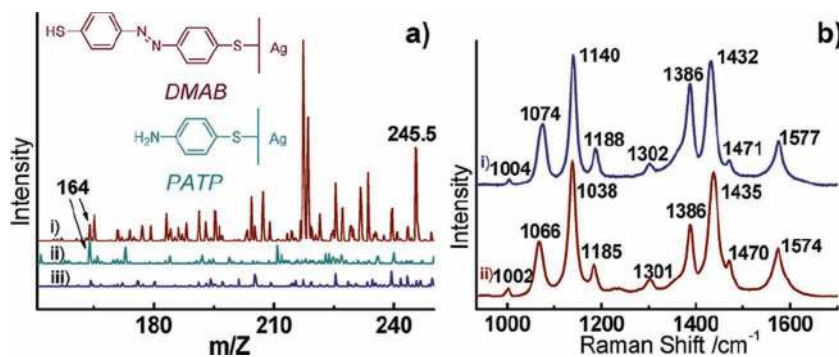
Figure 4. a) DESI (desorption electrospray inonization)-MS spectra of PATP adsorbed on roughened Ag electrodes, illuminated with laser light (i), without any irradiation (ii), and a roughened Ag-free spectrum of PATP (iii). b) The Raman spectrum of PATP (i), and DMAB (ii), on the roughened Ag electrode excited by laser light at a power density of ca. 1 × 10^8 mW/cm^2. Reproduced with permission.[21]Copyright 2010, American Chemical Society.

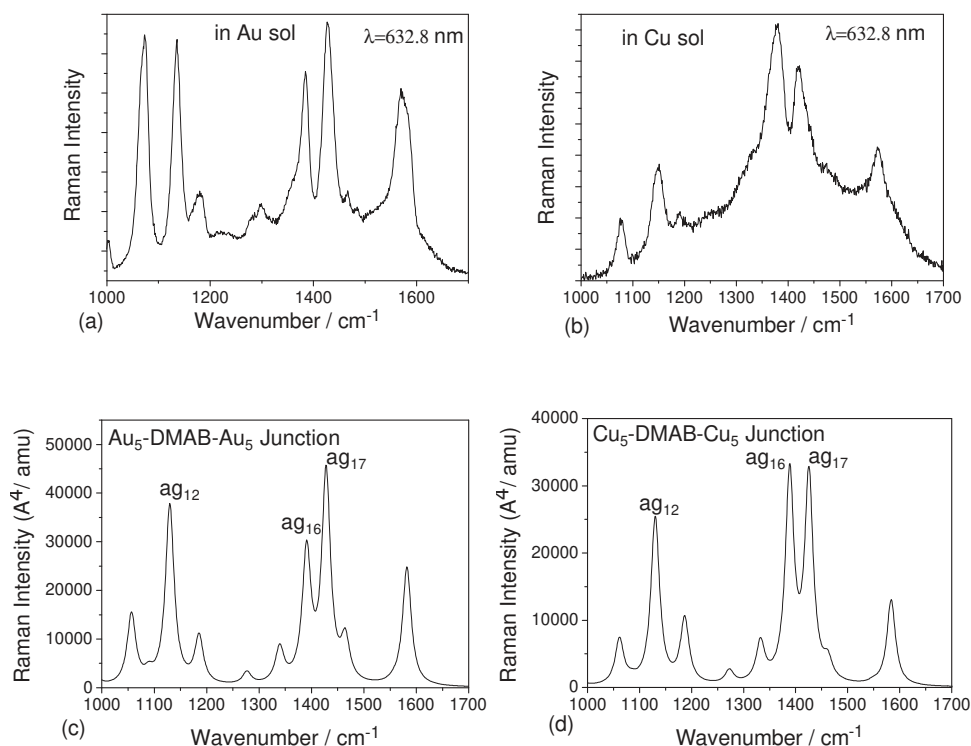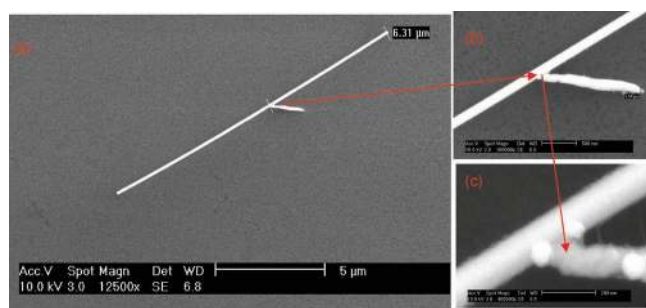**Figure 7.** a) SERS spectrum of DMAB in Au sol, b) SERS spectrum of DMAB in Cu sol, c) calculated SERS spectrum of DMAB in Au sol, and d) calculated SERS spectrum of DMAB in Cu sol. Reproduced with permission.[27] Copyright 2011, American Chemical Society.

will produced massive electromagnetic field enhancement for SERS measurement. **Figure 9**(a) reveals that SPPs can efficiently propagate along an Ag nanowire, and the propagating surface plasmons can be coupled out near the nanogap as a massive electromagnetic enhancement. Figure 9(b) shows remote SERS spectra of DMAB, produced from PATP by propagating surface plasmons, when the polarization angle is 0°. In our experiment, we first measured the remote SERS for the case of 0°, resulting in the strongest intensity of the SERS spectra, which is direct evidence for remote-excitation surface photochemical reactions. For other polarization angles, we assume that the measured Raman signal is from DMAB, since the PATP was catalyzed when we measured at the angle 0°.

Note that all of the experimental results were measured in neutral (pH = 7) environment in Refs. [20–22,24,26]. Recently,

the pH value effects on surface-catalyzed reactions were also investigated experimentally.[27–29] It is found that plasmon-assisted surface-catalyzed reactions can be efficiently controlled by different pH values. For pH = 10 in Au and Ag sol, we found that the Raman peaks for a_{g12}, a_{g16}, and a_{g17} vibrational modes are strongly enhanced (**Figure 10**(a) and (b), which confirmed experimentally that the surface-catalyzed reaction of DMAB produced from PATP occurred. For pH = 3 in Au and Ag sol (Figure 10(c) and (d)), we found that the Raman peaks for a_{g12}, a_{g16}, and a_{g17} vibrational modes were absent, and by comparing with Figure 10(e) and (f), they are similar to the simulated SERS spectra of PATP adsorbed on Au and Ag clusters, which means that under the condition of pH = 3, the surface-catalyzed reaction cannot happen. So, H⁺ and OH⁻ in the sols can control surface-catalyzed reactions.

Figure 8. a) SEM imaging of our system. b,c) Enlarged sections of (a). Reproduced with permission.[30] Copyright 2011, Springer.
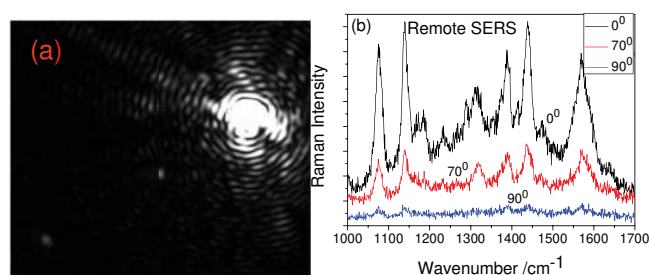

Figure 9. a) Optical image of SPPs propagating along a nanowire. b) Remote SERS spectra of DMAB with different angles between the polarization of the laser and the nanowire. Reproduced with permission.[30] Copyright 2011, Springer.
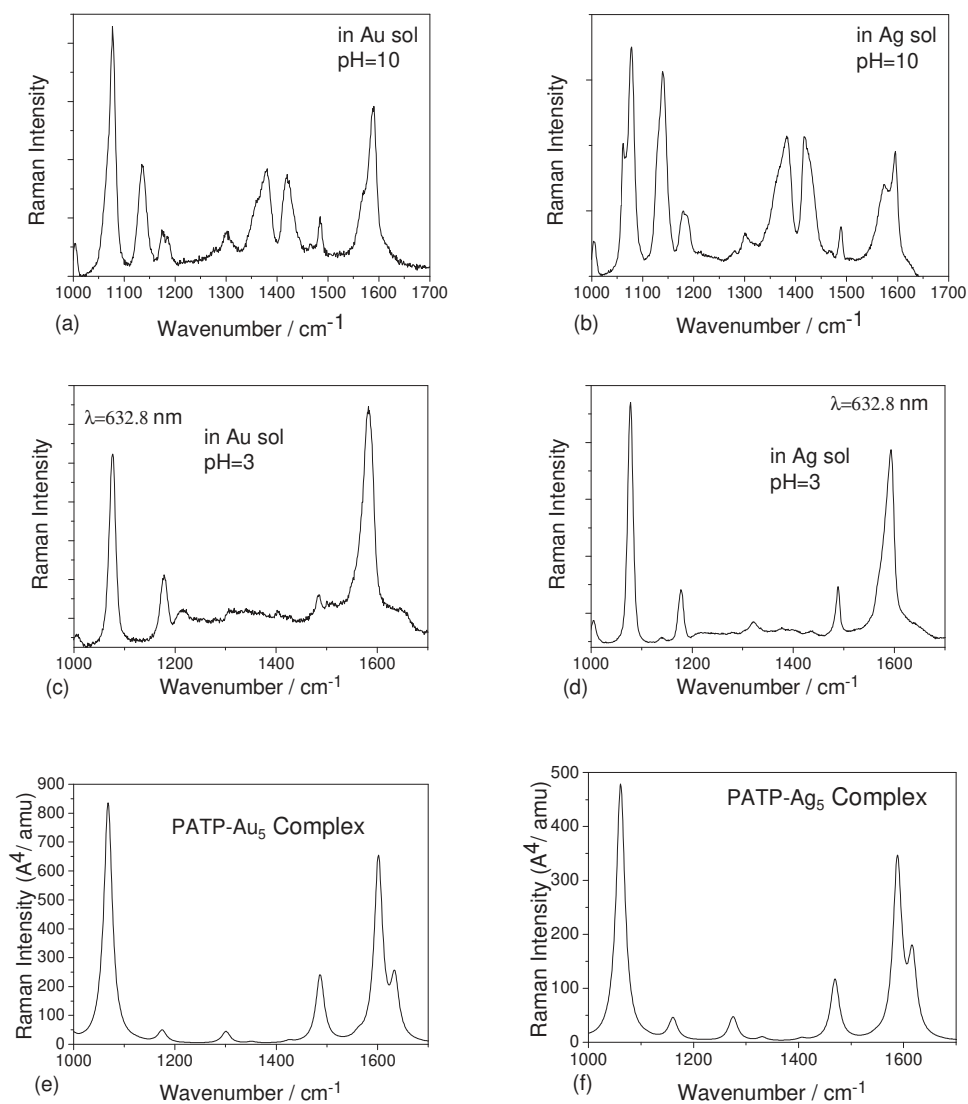
Figure 10. a) SERS spectrum of DMAB in Au sol (pH = 10), b) SERS spectrum of DMAB in Ag sol (pH = 10), c) SERS spectrum of PATP in Au sol (pH = 3), d) SERS spectrum of PATP in Ag sol (pH = 3), e) calculated SERS spectrum of PATP-Au$_5$ complex, f) calculated SERS spectrum of PATP-Ag$_5$ complex. Reproduced with permission.[27] Copyright 2011, American Chemical Society.

Furthermore, Gabudean et al., studied time-dependent pH controlled surface-catalyzed reactions. The SERS spectra (see **Figure 11**) measured after 15 days, illustrates an increasing intensity of peaks centered at 1139, 1392, and 1436 cm^{-1}. Even at pH ~ 7 and ~ 2, their contribution can be clearly distinguished in the spectrum. From the initial measurements at 2 h of incubation; no signal related to these three modes was detected. In the basic environment at pH ~ 11, these three modes were comparatively much stronger than those observed for the other pH values, suggesting an increased extent of DMAB formation. Zong et al.[28] has successfully fabricated a pH sensor, as an application of pH-sensing in a cell, based on PATP-functionalized HCl-treated gold nanorods (GNRs), using a SERS method. It can be used as a pH indicator by measuring the SERS signals of PATP-GNRs, because of the transformation of PATP molecules between two states under different pH conditions. In living cells, this type of pH sensor can deliver pH information of the surrounding environment.
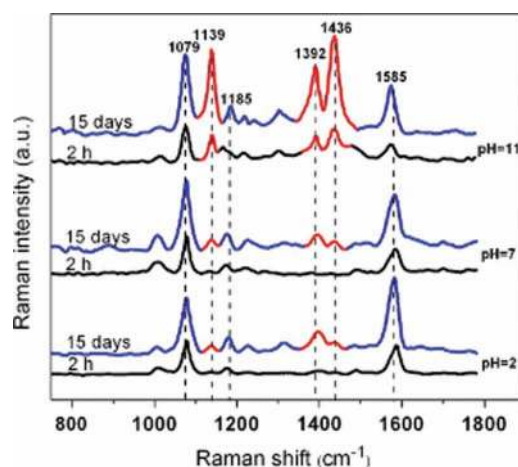
Figure 11. SERS spectra of p-ATP/GNRs conjugates in solutions at three different pH values, recorded 2 h and 15 days after the addition of p-ATP to a final concentration of 24 μм. Reproduced with permission.[29] Copyright 2010, Elsevier.
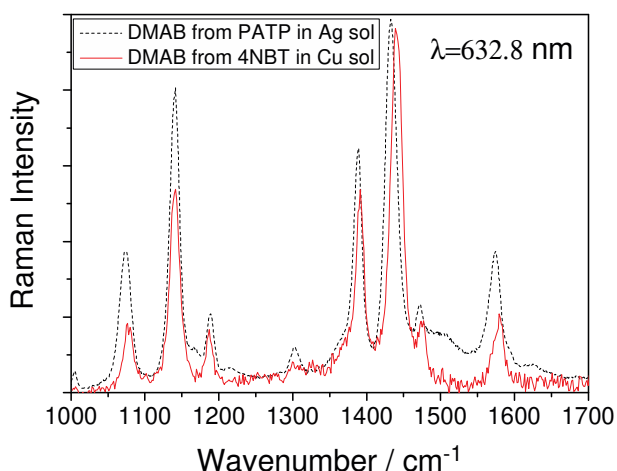
Figure 12. The experimental SERS of DMAB produced from PATP, and from 4-NBT by surface photochemistry reactions. Reproduced.[32]

2.3. Surface-Catalyzed Reactions of DMAB Produced from 4NBT Assisted by SPs

In our recent rapid communication,[32] we demonstrated that also a mixture of the nitro compounds related to PATP, i.e., 4-nitrobenzenethiol (4NBT), yields very similar SERS spectra (see **Figure 12**), which can be assigned to DMAB. This means that 4NBT is converted by a surface photochemical reaction to DMAB. It is a very important complement to our previous experimental study, showing that DMAB can be produced from PATP. We also experimentally investigated substrate-, wavelength-, and time-dependent plasmon-assisted surface photocatalyzed reactions of 4NBT dimerizing to DMAB on Au, Ag, and Cu films.[33] We found that surface-catalyzed reactions are strongly dependent on substrate, wavelength and time scale. It is revealed that the optimal experimental conditions can be rationally chosen to control (accelerate or restrain) these surface-catalyzed reactions. For this surface photocatalyzed reaction, on the Cu film for an incident light of 514.5 nm, the reaction time scale is within several minutes; and the reaction time scale is several hours on the Ag film (see **Figure 13**). There is no surface-catalyzed reaction on the Au film.
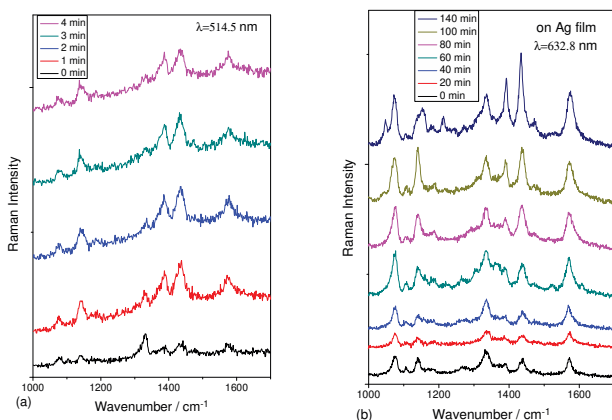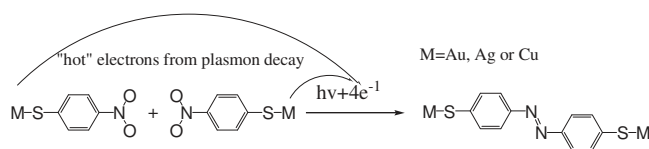

Figure 13. SERS spectra of 4NBT in the junction of Ag nanoparticle on Cu and Ag films, respectively. a) on Cu film with incident light of 514.5 nm, b) on Ag film with incident light of 632.8 nm. Reproduced with permission.[33] Copyright 2011, American Chemical Society.

Scheme 1. The mechanism of a plasmon-assisted surface-catalyzed reaction. Reproduced with permission.[33] Copyright 2011, American Chemical Society.

The mechanism[33] for the surface-catalyzed reaction of 4NBT converted to DMAB can be seen from **Scheme 1**. The four electrons ($4e^{-1}$), required in the chemical reaction, are proposed to be "hot electrons" arising from the surface plasmon decay.[89–92] The light quanta stored in the plasmons can be re-emitted as light, but some of the plasmons can also decay into two charge carriers, an electron and a "hole."[91] It has been known for some time that plasmon decay can create "hot" electrons that have high kinetic energy, which can presumably drive the surface-catalyzed reaction.[33] The provided experimental evidence for the surface-catalyzed reaction of 4NBT reducing to DMAB is very important, since the misunderstanding of 4NBT converting to PATP has been widely accepted by many groups.[93–100] It is necessary to correct this misunderstanding, and reveal the true nature of this surface-catalyzed reaction.

3. Conclusion and Outlook

Surface-catalyzed reactions of DMAB produced from PATP and 4NBT have been confirmed experimentally by local SPs, plasmonic waveguides, and theoretical simulations in 2010 and 2011. Significant progress has been made until now to further support and confirm these issues. It is confirmed that SERS is an invasive technique under certain conditions and, therefore, cannot obtain the vibrational fingerprint information of the original surface species. There is a new way to synthesize new molecules induced by local SPPs or propagating surface plasmons at the nanoscale. DMAB has been theoretically used as a molecule conductor in molecular electronics,[101] DMAB can be photosynthesized from PATP that was adsorbed on two leads by local SPs from Au leads. Surface-catalyzed reactions have also been used to detect the changes of environmental pH values in cells by local SPPs. We hope the environmental pH values in cells can also be detected by propagating surface plasmons, which can avoid higher power incident laser light, which causes cell destruction. Furthermore, it is expected that the molecules cannot only be synthesized, but can also be dissociated by local SPPs and propagating surface plasmons. For example, some molecules can contaminate the environment, and it is better that they can be dissociated by surface-catalyzed reactions induced by local SPPs or plasmonic waveguides. It is also a great challenge to investigate the time-dependent surface-catalyzed reaction induced by local SPPs and plasmonic waveguides, and faster surface photocatalytic reaction rates. To completely confirm that DMAB is produced from PATP by surface-catalyzed reactions, it is very important that the asymmetric b_u vibrational modes can

be observed experimentally. In SERS spectra of DMAB, the Raman intensities of these asymmetric b_u vibrational modes are zero, while they can be observed experimentally in HV-TERS.[22] In HV-TERS, plasmon-driven catalyzed reactions can be rationally controlled by the incident laser intensity, current, and voltage. It is expected that further works on plasmon-driven surface-catalyzed reactions can be performed in HV-TERS.

Acknowledgements

[1] R. H. Ritchie, *Phys. Rev.* **1957**, *106*, 874.
[2] J. M. Brockman, B. P. Nelson, R. M. Corn, *Annu. Rev. Phys. Chem.* **2000**, *51*, 41.
[3] S. P. Zhang, K. Bao, N. J. Halas, H. X. Xu, P. Nordlander, *Nano Lett.* **2011**, *11*, 1657.
[4] H. X. Xu, E. J. Bjerneld, M. Kail, L. Borjesson, *Phys. Rev. Lett.* **1999**, *83*, 4357.
[5] A. V. Akimov, A. Mukherjee, C. L. Yu, D. E. Chang, A. S. Zibrov, P. R. Hemmer, H. Park, M. D. Lukin, *Nature* **2007**, *450*, 402.
[6] N. Fang, H. Lee, C. Sun, X. Zhang, *Science* **2005**, *308*, 534.
[7] Z. W. Liu, H. Lee, Y. Xiong, C. Sun, X. Zhang, *Science* **2007**, *315*, 1686.
[8] H. J. Lezec, N. A. Dionne, H. A. Atwater, *Science* **2007**, *316*, 430.
[9] N. Engheta, *Science* **2007**, *317*, 1698.
[10] Y. Fang, Z. Li, Y. Huang, S. Zhang, P. Nordlander, N. J. Halas, H. X. Xu, *Nano Lett.* **2010**, *10*, **1950**.
[11] H.Wei, Z. Li, X. Tian, Z. Wang, F. Cong, N. Liu, S. Zhang, P. Nordlander, N. J. Halas, H. X. Xu, *Nano Lett.* **2011**, *11*, 471.
[12] T. Ergin, N. Stenger, P. Brenner, J. B. Pendry, M. Wegener, *Science* **2010**, *328*, 337.
[13] S. Lal, S. E. Clare, N. J. Halas, *Acc. Chem. Res.* **2008**, *41*, 1842.
[14] M. Ozaki, J. Kato, S. Kawata, *Science* **2011**, *332*, 218.
[15] Y. Tsuboi, R. Shimizu, T. Shoji, N. Kitamura, *J. Am. Chem. Soc.* **2009**, *131*, 12623.
[16] K. Ueno, S. Juodkazis, T. Shibuya, Y. Yokota, V. Mizeikis, K. Sasaki, H. Misawa, *J. Am. Chem. Soc.* **2008**, *130*, 6928.
[17] C. Deeb, C. Ecoffet, R. Bachelot, J. Plain, A. Bouhelier, O. Soppera, *J. Am. Chem. Soc.* **2011**, *133*, 10535.
[18] C. Hubert, A. Rumyantseva, G. Lerondel, J. Grand, S. Kostcheev, L. Billot, A. Vial, R. Bachelot, P. Royer, S.-H. Chang, S. K. Gray, G. P. Wiederrecht, G. Schatz, *Nano Lett.* **2005**, *5*, 615.
[19] C. J. Chen, R. M. Osgood, *Phys. Rev. Lett.* **1983**, *50*, 1705.
[20] Y. Fang, Y. Li, H. X. Xu, M. T. Sun, *Langmuir* **2010**, *26*, 7737.
[21] Y. F. Huang, H. P. Zhu, G. K. Liu, D. Y. Wu, B. Ren, Z. Q. Tian, *J. Am. Chem. Soc.* **2010**, *132*, 9244.
[22] M. T. Sun, Y. R. Fang, Z. Y. Zhang, H. X. Xu, arXiv:1112.4218v1.
[23] D. Y. Wu, X. M. Liu, Y. F. Huang, B. Ren, X. Xu, Z. Q. Tian, *J. Phys. Chem. C* **2009**, *113*, 18212.
[24] V. Canpean, M. Iosin, S. Astilean, *Chem. Phys. Lett.* **2010**, *500*, 277.
[25] D. Y. Wu, L. B. Zhao, X. M. Liu, R. Huang, Y. F. Huang, B. Ren, Z. Q. Tian, *Chem. Commun.* **2011**, *47*, 2520.
[26] Y. Z. Huang, Y. R. Fang, Z. L. Yang, M. T. Sun, *J. Phys. Chem. C* **2010**, *114*, 18263.
[27] M. Sun, Y. Huang, L. Xia, X. Chen, H. Xu, *J. Phys. Chem. C* **2011**, *115*, 9629.
[28] S. Zong, Z. Wang, J. Yang, Y. Cui, *Anal. Chem.* **2011**, *83*, 4178.
[29] A. M. Gabudean, D. Biro, S. Astilean, *J. Mol. Struct.* **2011**, *993*, 420
[30] M. T. Sun, Y. Hou, Z. Li, L. Liu, H. Xu, *Plasmonics*, **2011**, *6*, 681.
[31] M. T. Sun, Y. X. Hou, H. X. Xu, *Nanoscale*, **2011**, *3*, 4114.
[32] B. Dong, Y. R. Fang, L.X. Xia, H. Xu, M. T. Sun, *J. Raman Spectrosc.* **2011**, *42*, 1205.
[33] B. Dong, Y. R. Fang, X. W. Chen, H. X. Xu, M. T. Sun, *Langmuir*, **2011**, *27*, 10677.
[34] A. Furube, K. Hara, R. Katoh, M. Tachiya, *J. Am. Chem. Soc.* **2007**, *129*, 14852.
[35] H. Zhu, X. Ke, X. Yang, S. Sarina, H. Liu, *Angew. Chem. Int. Ed.* **2010**, *49*, 9657.
[36] P. Christopher, H. Xin, S. Linic, *Nature Chem.* **2011**, *3*, 467.
[37] S. Linic, P. Christopher, D. B. Ingram, *Nature Materials*, **2011**, *10*, 911.
[38] T. Wadayama, M. Yokawa, *Chem. Phys. Lett.* **2006**, *428*, 348.
[39] M. Muniz-Miranda, B. Pergolese, A. Bigotto, *J. Phys. Chem. C* **2008**, *112*, 6988.
[40] S. Navalon, M. de Miguel, R. Martin, M. Alvaro, H. Garcia, *J. Am. Chem. Soc.* **2011**, *133*, 2218.
[41] P. Gao, D. Gosztola, M. J. Weaver, *J. Phys. Chem.* **1988**, *92*, 7122.
[42] C. G. Silva, R. Juárez, T. Marino, R. Molinari, H. García, *J. Am. Chem. Soc.* **2011**, *133*, 595.
[43] S. Gao, K. Ueno, H. Mishwa, *Acc. Chem. Res.* **2011**, *44*, 251.
[44] S. N. Maximoff, M. P. Head-Gordon, *PNAS*, **2009**, *106*, 11460.
[45] M. Fleischmann, P. J. Hendra, A. J. McQuillan, *Chem. Phys. Lett.* **1974**, *26*, 163.
[46] D. L. Jeanmaire, R. P. Van Duyne, *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *84*, 1.
[47] M. Moskovits, *Rev. Mod. Phys.* **1985**, *57*, 783.
[48] H. Metiu, P. Dos, *Annu. Rev. Phys. Chem.* **1984**, *35*, 507.
[49] K. Kneipp, H. Kneipp, I. Itzkan, R. R. Dasari, M. S. Feld, *Chem. Rev.* **1999**, *99*, 2957.
[50] J. R. Lombardi, R. L. Birke, *Acc. Chem. Res.* **2009**, *42*, 734.
[51] L. L. Zhao, L. Jensen, G. C. Schatz, *J. Am. Chem. Soc.* **2006**, *128*, 2911.
[52] A. Otto, *J. Raman Spectrosc.* **2005**, *36*, 497.
[53] J. R. Lombardi, R. L. Birke, *J. Phys. Chem. C* **2008**, *112*, 5605.
[54] B. Dong, L. Liu, H. Xu, M. T. Sun, *J. Raman Spectrosc.* **2010**, *41*, 719.
[55] M. T. Sun, S. S. Liu, M. D. Chen, H. X. Xu, *J. Raman Spectrosc.* **2009**, *40*, 137.
[56] W. Hill, B. Wehling, *J. Phys. Chem.* **1993**, *97*, 9451.
[57] M. Osawa, N. Matsuda, K. Yoshii, I. Uchida, *J. Phys. Chem.* **1994**, *98*, 12702.
[58] L. Cao, P. Diao, L. Tong, T. Zhu, Z. F. Liu, *ChemPhysChem* **2005**, *6*, 913.
[59] J. W. Gibson, B. R. Johnson, *J. Chem. Phys.* **2006**, *124*, 064701.
[60] D. P. Fromm, A. Sundaramurthy, A. Kinkhabwala, P. J. Schuck, G. S. Kino, W. E. Moerner, *J. Chem. Phys.* **2006**, *124*, 061101.
[61] Q. Zhou, X. W. Li, Q. Fan, X. X. Zhang, J. W. Zheng, *Angew. Chem. Int. Ed.* **2006**, *45*, 3970.
[62] Q. Zhou, G. Zhao, Y W. Chao, Y. Li, Y. Wu, J. W. Zheng, *J. Phys. Chem. C* **2007**, *111*, **1951**.
[63] F. Toderas, M. Baia, L. Baia, S. Astilean, *Nanotechnology* **2007**, *18*, 255702.
[64] Y. L. Wang, X Q. Zou, W. Ren, W. D. Wang, E. K. Wang, *J. Phys. Chem. C* **2007**, *111*, 3259.
[65] Q. Zhou, Y. W. Chao, Y. Li, W. Wu, Y. Wu, J W. Zheng, *ChemPhysChem* **2007**, *8*, 921.
[66] S. S. Liu, X. M. Zhao, Y. Z. Li, X. H. Zhao, M. D. Chen, *J. Chem. Phys.* **2009**, *130*, 234509.
[67] G. K. Liu, J. Hu, P. C. Zheng, G. L. Shen, J. H. Jiang, R. Q. Yu, Y. Cui, B. Ren, *J. Phys. Chem. C* **2008**, *112*, 6499.
[68] Z. Sun, C. Wang, J. Yang, B. Zhao, J. R. Lombardi, *J. Phys. Chem. C* **2008**, *112*, 6093

[69] N. Zhao, Y. Wei, N. Sun, Q. Chen, J. Bai, L. Zhou, Y. Qin, M. Li, L. Qi, *Langmuir*, **2008**, *24*, 991.

[70] Y. Qin, Y. Song, T. Huang, L. Qi, *Chem. Commun.* **2011**, *47*, 2985.

[71] A. P. Richter, J. R. Lombardi, B. Zhao, *J. Phys. Chem. C,* **2010**, *114*, 1610.

[72] L. Wang, H. Li, J. Tian, X. Sun, *ACS Appl. Mater. & Inter.* **2011**, *2*, 2987.

[73] J. R. Lombardi, R. L. Birke, G. Haran, *J. Phys. Chem. C* **2011**, *115*, 4540.

[74] Y. Zhang, S. Liu, L. Wang, X. Y. Qin, J. Tian, W. Lu, G. Chang, X. Sun, *RSC Advances* **2012**, *2*, 538.

[75] A. Sugie, K. Kumazawa, T. Hatta, K. Kanie, A. Muramatsu, A. Mori, *Chem. Lett.* **2011**, *40*, 1450.

[76] W. H. Park, Z. H. Kim, *Nano Lett.* **2010**, *10*, 4040.

[77] K. Kim, J. K. Yoon, H. B. Lee, D. Shin, K. S. Shin, *Langmuir* **2011**, *27*, 4526.

[78] K. Kim, D. Shin, H. B. Lee, K. S. Shin, *Chem. Commun.* **2011**, *47*, 2020.

[79] K. Kim, H. B. Lee, D. Shin, H. Ryoo, J. W. Lee, K. S. Shin, *J. Raman Spectrosc.* **2011**, *42*, 2112.

[80] X. Wang, W. Shi, G. She, L. Mu, *J. Amer. Chem. Soc.* **2011**, *133*, 16518.

[81] K. Ikeda, S. Suzuki, K. Uosaki, *Nano Lett.* **2011**, *11*, 1716.

[82] L. Yang, L. Ma, G. Chen, J. Liu, Z. Q. Tian, *Chem. Eur. J.* **2010**, *16*, 12683.

[83] C. Farcau, S. Astilean, *Chem. Comm.* **2011**, *47*, 3861.

[84] D. R. Ward, N. J. Halas, J. K. Ciszek, J. M. Tour, Y. Wu, P. Nordlander, D. Natelson, *Nano Lett.* **2008**, *8*, 919.

[85] X. M. Yang, D. A. Tryk, K. Ajito, K. Hashimoto, A. Fujishima, *Langmuir* **1996**, *12*, 5525.

[86] X. M. Yang, D. A. Tryk, K. Hashimoto, A. Fujishima, *J. Raman Spectrosc.* **1998**, *29*, 725.

[87] R. M. Dickson, L. A. Lyon, *J. Phys. Chem. B* **2000**, *104*, 6095

[88] Y. Fang H. Wei, F. Hao, P. Nordlander, H. X. Xu, *Nano Lett.* **2009**, *9*, 2049.

[89] Y. Huang, Y. Fang, M. T. Sun, *J. Phys. Chem. C* **2011**, *115*, 3558.

[90] M. W. Knight, H. Sobhani, P. Nordlander, N. Halas, *J. Science* **2011**, *332*, 702.

[91] M. Moskovits, *Science*, **2011**, *332*, 676.

[92] V. M. Shalaev, C. Douketis, J. T. Stuckless, M. Moskovits, *Phys. Rev. B* **1996**, *53*, 11388.

[93] K. Kim, Y. M. Lee, H. B. Lee, Y. Park, T. Y. Bae, Y. Jung, C. H. Choi, K. S. Shin, *J. Raman Spectrosc.* **2010**, *41*, 187.

[94] K. S. Shin, H. S. Lee, S. W. Joo, K. Kim, *J. Phys. Chem. C* **2007**, *111*, 15223.

[95] K. Kim, H. S. Lee, *J. Phys. Chem. B* **2005**, *109*, 18929.

[96] K. Kim, I. Lee, S. J. Lee, *Chem. Phys. Lett.* **2003**, *377*, 201.

[97] S. J. Lee, K. Kim, *Chem. Phys. Lett.* **2003**, *377*, 122.

[98] S. W. Han, I. Lee, K. Kim, *Langmuir* **2002**, *18*, 182.

[99] K. Kim, I. Lee, *Langmuir* **2004**, *20*, 7351.

[100] Y. C. M. Liou, J. Yang, A. Fasasi, P. R. Griffiths, *Appl. Spectrosc.* **2011**, *65*, 528.

[101] R. Turansky, M. Konpka, N. L. Doltsinis, I. Stich, D. Marx, *ChemPhysChem* **2010**, *11*, 345.