

This chapter discusses the fundamentals of the surface-enhanced Raman scattering (SERS) effect. SERS consists in using the large local field enhancements that can exist at metallic surfaces (under.

This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. Received May 29, ; revised June 31, ; accepted July 27, Keywords: Therefore, Surface Enhanced Raman Spectroscopy SERS based on the adsorption of organic analytes onto gold or silver nanostructures has been used to enhance the signal of chemicals presented at very low concentrations. Although the plasmonic effect of SERS has been shown to play a large role in signal enhancement, the significance of the chemical effect due to the analyte chemisorption on the gold or silver surface is less well understood. In this study, the role of aniline substituents is examined by probing the SERS intensities of various anilines in silver and gold colloids using a Raman spectrometer with an excitation wavelength of nm. The SERS enhancement factors and detection limits for aniline and its mono and di-substituted ortho derivatives are determined and compared. Both the steric requirements of chemisorption and the inductive effects of electron-withdrawal due to the substituents affect the signal intensities of various vibrational modes of the amino group and the aromatic ring. The degree of enhancement is also related to the methods for preparing the silver and gold colloids, which are characterized by probing the nanoparticle morphology and its degree of aggregation using transmission electron microscopy TEM. Introduction The SERS effect for amplifying the Raman signal via analyte adsorption onto gold or silver is based on two separate phenomena of electromagnetic and chemical enhancement. The electromagnetic enhancement effect based primarily on the excitation of localized surface plasmons in metallic nanostructures has been reported to be more significant than the chemical enhancement as a result of chemisorption via specific functional groups of the adsorbed molecules [1]. Many studies have focused on the investigation of the plasmonic effect based on the most SERS-active compounds, such as RhodamineG and Malachite Green [2,3], and have demonstrated SERS enhancement factors of greater than The chemical enhancement effect, based on the molecular structures and the functional groups of the adsorbed compound, is not as well understood, and is probed in this research study. Aniline, as an aromatic amine, is a useful compound for demonstrating the significance of the chemical enhancement effect. This is due to interactions between the noble metal and the lone pair of electrons on the amino group, as well as interactions between the aromatic ring and the metal. Previous studies have identified both electron withdrawing character and steric hindrance as affecting chemical enhancement by the addition of substituent groups in the ortho, meta, and para positions [4]. The position of the substituent group on the ring will impact the electron withdrawing strength, the dipole moment of the molecule and also its induced dipole moment. Since both the inherent dipole and the induced dipole moment of a molecule is associated with their polarizability due to the electric field produced by the surface plasmon of the metal, the orientation of the adsorbed molecules and their vibrational modes are greatly affected in SERS. Calculation conducted for o-, m-, and p-nitroaniline using the density functional theory DFT method have predicted that o-nitroaniline and p-nitroaniline have different adsorption orientations on the metal [5] due to the position of the nitro group on the aromatic ring. Both computational modeling and SERS studies of anilines have focused primarily on anilines with para-substituents [] because of the industrial importance of anilines. In order to elucidate the role of chemical enhancement due to different functional groups in the ortho position of anilines, SERS studies are conducted for investigating how the steric and electronic effects of the ortho substituents would influence the charge transfer between specific anilines and metal through their interactions between the amino group or the aromatic ring of aniline and the metal. The magnitude of the SERS enhancement factors for various ortho-substituted anilines can be attributed to strength of the charge transfer interactions between the adsorbed analytes and the silver or gold colloids and correlated to affinity for electron donation based on their pKa

values. The outcome of this study will contribute to the possible application of SERS for environmental monitoring of anilines. Materials and Methods 2. The deionized water has a resistivity of greater than 18 megaohm-cm. Synthesis of Colloidal Gold and Silver Colloidal silver nanospheres were prepared using the Leopold and Lendl method [9] by rapidly mixing 90 mL of 1. Colloidal gold nanostars were prepared by the Xie et al. The reaction was allowed to proceed without shaking or stirring for 20 minutes, during which a color change to colorless followed by dark purple occurred. The lower concentrations used for SERS measurements were prepared by diluting the stock solutions. Samples were prepared using a 1 to 9 volume ratio of analyte in acetonitrile to silver colloid and 1 to 1 volume ratio of analyte in deionized water to the colloidal gold nanostars. The Raman spectra were collected while the sample was wet and also after it was dried. The laser excitation beam was focused at the periphery of the dried sample spots with a probe-to-sample distance of 7 mm. Irvine, CA at a wavelength of nm. The peak areas of the 1 - 3 most intense SERS peaks were used for the calculation of SERS enhancement factors using the integration tool in OMNIC and peak-to-peak noise was used for calculation of the minimum detection limits of analytes based on the 3-sigma definition. Transmission Electron Microscopy The TEM specimens for the characterization of particle size and morphology of colloidal gold nanostars were prepared as follows. Alternatively, the carbon-coated grids were held with a pair of tweezers along the path traveled by the mist produced by the nebulizer at approximately 10 cm from the nozzle. These nebulization procedures allowed uniform deposition of gold and silver nanoparticles onto the carbon-coated grids. Data Analysis The SERS enhancement factors were calculated using the Equation 1 by comparing the relative sensitivity of each compound for SERS versus normal Raman signals for spectral signals associated with specific vibrational modes. The Raman spectrometer conditions of laser power and signal integration period were kept constant for both SERS and normal Raman measurements. For almost all spectral peaks of all compounds studied, the wavenumber of the peaks for a specific vibrational mode will be similar for both SERS and normal Raman spectra. Therefore, only in the case of the NH₂ wagging mode for aniline, the large peak shift *i*. The LOD values shown in Table 1 are equivalent to the lowest analyte concentrations that gives peak areas corresponding to three times their respective background noise or standard deviation of the background signals. Results and Discussions 3. The three most prominent spectral peaks, labeled for each spectrum, were used to determine the enhancement factors tabulated in Table 2. The enhancement factor for the NH₂ stretching vibrational mode is calculated to be 2. The gold colloid was found to yield stronger signals than the silver colloid at the same aniline concentration. In general the enhancement factors for gold are better than those for silver as reported previously [12]. One possible explanation, based on work done by Zhao et al. Limits of Detection LOD for aniline and selected anilines in gold and silver colloids. The normal Raman spectrum was obtained for aniline at 20, ppm, whereas the SERS spectrum for aniline was obtained for a sample prepared by mixing 10, ppm aniline with silver colloid at a 1: The SERS spectrum based on gold nanostars was obtained for a sample of 6 ppm aniline mixed with the colloid at a 1: All spectra were acquired for seconds. Besides, the silver colloid requires an extra step of pre-concentration to give larger signal enhancement. The SERS spectra for aniline in gold and silver colloids are very similar. In this study, anilines with alkyl groups in the ortho position are investigated with regard to their roles in the SERS enhancement effects. The *t*-butyl group was more effective in suppressing both the NH₂ wagging and scissoring modes. Furthermore, the presence of two isopropyl groups at the ortho positions of aniline also prevents the molecule from contorting itself in forming a charge-transfer bond as is possible with 2-isopropylaniline. The Steric and Electron-Withdrawal Effects of Halogen Substituent Groups on SERS Signals of Anilines The electron withdrawing effects of halogens due to their different electronegativity values along with their trends in atomic radii is well known in chemistry. For the mono-halogenated anilines, the influence of electron withdrawal generally makes it less likely for the amino groups to interact or donate electrons to the silver or gold nanoparticles. The presence of both bromine and iodine substituents drastically decreases the analytical sensitivity of these aniline derivatives, resulting in their higher detection limits Table 1. The presence of two halogen substituents in both ortho positions of anilines further reduces the intensities of

Figure 2. Colloidal gold nanostars were mixed with aqueous standards at 1: The initial concentrations of the standards were 6. Spectra were obtained by mixing aqueous standards with gold colloid in 1: The initial concentrations of the standards were ppm for 2-fluoroaniline, ppm for 2-chloroaniline, ppm for 2-bromoaniline, and ppm for 2-iodoaniline. SERS signals while showing similar shift to lower wavenumbers for specific vibrational modes as shown in Figure 4. Besides showing a smaller Raman intensity scale relative to the mono-halogenated anilines, the dihalogenated aniline derivatives also shows higher fluorescence background. This effect was most clearly observed for the plot with data for aniline, three alkyl anilines, and its nitro and dinitro derivatives. The nature of the aniline chemisorption on metals is Figure 4. Spectra were obtained for samples prepared by mixing aqueous standards with gold colloid in 1: The initial analyte concentrations were ppm for 2,6-difluoroaniline, ppm for 2,6-dichloroaniline, and 75 ppm for 2,6-dibromoaniline. Therefore, it is reasonable to expect that pKa values of aniline and its derivatives to be related to their enhancement factors. However, it is also important to recognize that the degree of enhancement is also related to the compatibility of energy levels between the aniline derivatives and the metal surfaces. It is beneficial to further explore computational modeling to predict the effects of various aniline substituents on their physical properties including acidity or pKa. Previous studies have shown that charge distribution in anilines and the charge density on the nitrogen of the amino group in anilines can affect the acidity of aniline and its derivatives [16,17].

TEM Characterization of Gold Nanostars The nanoparticle morphology in the gold or silver colloids greatly influences the magnitude of signal enhancement as previously noted for nanospheres, nanorods, nanowires, and nanostars [18]. X-ray microanalysis was used to confirm the gold elemental signal of the nanoparticles. The numbers of nanoparticles for each aggregated cluster is significantly larger than those observed for silver colloids obtained by the method of Lendl and Leopold [9]. The nanoparticle size is in the range of 10 - 30 nm and the number of particles per cluster is estimated in the range of 20 - 60, which is much larger than the nanosphere clusters of gold and silver reported earlier [14]. This implies that all the particles observed in Figure 6 a were contained in a one single aerosol droplet. As the aqueous solvent evaporated, the distinct clusters overlapped to varying extent. The estimation of the ratio of nanostars to nanospheres on the 2-dimensional TEM image is difficult due to significant aggregation and stacking of nanoparticles. In Figure 6 b , isolated nanostars along with nanospheres were imaged at ,fold magnification and a b Figure 6. Among all these parameters, the branch length or L is the most significant in influencing the SERS intensities since the localized surface plasmon resonance effect is concentrated at the branches, especially their tips. Based on the ratio of nanostars to nanospheres observed in TEM, it is likely that the SERS enhancement can be improved further by varying the concentration of gold III chloride solution to maximize the production of nanostars and to increase the length of the nanostar branches. The nebulization of colloidal samples onto carboncoated grids was found to be a suitable sample preparation method for TEM imaging of metal nanoparticles. The ability to gently deposit the particles without rupturing the carbon film on the TEM grid along with the quick evaporation of the solvent mostly in the gas phase allow the observation of nanoparticles as close to their native state of colloidal dispersion. The variables of the grid exposure time and the distance between TEM grid and nebulizer nozzle have to be controlled for optimal coverage of grid with nanoparticles, which were found to be 40 - 60 seconds and 7 - 10 cm, respectively. Potential Applications of SERS Technique for Monitoring Anilines Anilines are an important class of compounds widely used in industries, especially as a precursor for making dyes for fabric, leather, and other consumer goods. Workers in manufacturing industries involved in the production and use of dyes face occupational risk in being exposed to harmful levels of aromatic amines including anilines. Therefore, a robust and inexpensive method for screening or monitoring these compounds are highly desired for human health protection. Although aniline is the most important member of all the aniline compounds in terms of production volume and toxicological importance, other anilines are also included in this study for a more comprehensive evaluation of the feasibility of the SERS technique for analyzing samples with aniline and aniline derivatives. The limits of detection LODs were calculated for selected ortho-substituted anilines. Since the substituents of these anilines

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either exert the inductive effect of electron withdrawal from the amino group i. Other LODs for aniline derivatives are higher than those of aniline because the ortho substituents either pose a steric constraint or inductive effect of electron withdrawal that preclude effective chemisorption of the compounds via the amino group. Compounds such as the di-halogenated anilines as well as the mono and di-nitroanilines exhibit high levels of fluorescence background when silver colloid is used and hence their LOD values are generally higher than the non-fluorescent compounds. Both the enhancement factors Table 2 and LODs show that the steric hindrance for the bulky tertiary-butyl group is more significant than the isopropyl group in the ortho position, a notion expressed in the paper by Ikezawa et al. Conclusion This study is designed to investigate the variables influencing the magnitude of SERS enhancement factors. It was found that gold nanostar is more effective than the silver nanospheres in enhancing the SERS signals of anilines. The substituents at the ortho position of anilines also lower the pKa values to different extent such that high enhancement factors are strongly correlated with high pKa values.

Chapter 2 : Principles of Surface-Enhanced Raman Spectroscopy and Related Plasmonic Effects - Knowel

It addresses the issues such as how much the signal can be boosted, i.e. to know what the enhancement factor is, and what its physical origins are, by defining rigorously the SERS enhancement factors, and then by discussing their origin, with a strong emphasis on the electromagnetic (EM) mechanisms.

Find articles by Alan X. Received Apr 14; Accepted May This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license <http://creativecommons.org/licenses/by/4.0/>: This article has been cited by other articles in PMC. Abstract Surface-enhanced Raman scattering SERS has demonstrated single-molecule sensitivity and is becoming intensively investigated due to its significant potential in chemical and biomedical applications. SERS sensing is highly dependent on the substrate, where excitation of the localized surface plasmons LSPs enhances the Raman scattering signals of proximate analyte molecules. This paper reviews research progress of SERS substrates based on both plasmonic materials and nano-phonic structures. We first discuss basic plasmonic materials, such as metallic nanoparticles and nano-rods prepared by conventional bottom-up chemical synthesis processes. Then, we review rationally-designed plasmonic nano-structures created by top-down approaches or fine-controlled synthesis with high-density hot-spots to provide large SERS enhancement factors EFs. Finally, we discuss the research progress of hybrid SERS substrates through the integration of plasmonic nano-structures with other nano-phonic devices, such as photonic crystals, bio-enabled nanomaterials, guided-wave systems, micro-fluidics and graphene. Introduction The first observation of enhanced Raman spectra of pyridine on rough silver film was reported in [1], but the increment of Raman signals was incorrectly attributed to a larger number of molecules on the corrugated surface of the electrode. In , Van Duyne and Albrecht discovered surface-enhanced Raman scattering SERS [2 , 3] as a new phenomenon with extraordinary enhancement of Raman signals from molecules that are in the proximity of metallic nanostructures. Since then, the research interest of SERS has witnessed exponential expansion over the past 38 years, benefitting from a series of discoveries, theories and technological advancements [4 , 5 , 6]. In the most recent decade, the explosion of SERS research has majorly been driven by the rapid progress of nanotechnologies [7 , 8 , 9] and the incentives for chemical and biomedical applications [10 , 11 , 12 , 13], all of which have greatly fueled the current research endeavors in this topic. As a highly-sensitive vibrational spectroscopy that allows for the detection of analytes at extremely low concentrations [14 , 15 , 16 , 17], SERS probes the vibrational spectra of various molecules through the enhancement of metallic nanostructures. In general, there are two important mechanisms underlying SERS [18 , 19]. The first and also the dominant mechanism towards large EF is due to the electromagnetic field enhancement [20 , 21], where localized surface plasmons LSPs of metallic nanostructure increase the Raman signal intensity. The other contribution to SERS EFs is due to the chemical enhancement mechanism [23 , 24], where the charge transfer mechanism between the adsorbed molecule and metal plays a critical role in enhancing and modifying the modes of molecular vibration. Theoretically, chemical EFs up to were calculated using time-dependent density functional theory for para- and meta-substituted pyridine interacting with a silver cluster, but were highly molecular dependent [25 , 26]. Any molecule in an SERS-active hot-spot will exhibit an enormous enhancement in its Raman scattering signals.

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Chapter 3 : Surface-enhanced Raman spectroscopy - Wikipedia

s of surface-enhanced Raman spectroscopy and related plasmonic effects Eric C. Le Ru and Pablo G. Etchegoin SERS enhancement factors and related topics 4. 1.

SERS and the rise of the Raman empire By Dermot Martin 16 December No comments Dermot Martin looks at how SERS was invented and how it is expanding its sphere of influence. It might not generate the same headlines as stunning images from Pluto or the latest discovery from the Large Hadron Collider, but laser Raman spectroscopy does occasionally appear as a blip on the news agenda. Last summer it attracted media attention in the case of Reuben Hill, a cancer patient in the UK who had brain cancer cells identified by the method and removed during surgery – when he was fully conscious and even able to sing during the operation. We should remember that the discovery of surface-enhanced Raman spectroscopy (SERS) was a historic breakthrough which has been helping save lives in the field of healthcare and finding use in applications such as medical diagnostics, food safety, national security, environmental monitoring, fine art preservation, financial security and rapid screening. It deserves more recognition. Away from the public gaze, SERS gives chemists a priceless insight into the nature of atoms and how they interact. But how did this technique come about? This potentially opened up a direct and instantaneous route to identifying single molecules. Rough road After more than four decades of research and more than 12,000 publications on the topic, there is still no complete agreement on what the precise mechanism is for SERS. US-based scientists Richard Van Duyne at Northwestern University in Evanston, Illinois, and Martin Moskovits at the University of California, Santa Barbara, have spent their careers developing different techniques for SERS looking for new applications and building teams of researchers to seek answers to the mechanism of the phenomenon. It was Van Duyne who first used the term SERS. His SERS journey began in the early 1970s when working on the problem of the low signal output from Raman interactions with pyridine. He tried several approaches with argon laser light, but even with what was then state-of-the-art equipment he could not capture a decent output signal. In April 1977, he was working on obtaining the resonance Raman spectra of molecules adsorbed on the surface of electrodes. They had observed count rates of about 10³ per second using 10 mW of laser light. Jim himself thought surface roughness was likely to be the key factor. Was it all down to surface area effect as Fleischmann accepted, or was there some other, as yet hidden, explanation? They carried out their own series of experiments to measure the surface enhancement factor that compared the signal intensity per molecule on the surface to the signal intensity per molecule for the same molecule in free solution and discovered a 10⁶ enhancement factor associated with SERS. This result could not be explained by a surface area hypothesis. These two ideas, the electromagnetic and chemical enhancement mechanisms, have always rubbed against each other in mechanistic debate. It still causes friction today whenever it is discussed. But there is now general acceptance that SERS relies on an electrostatic plasmonic effect in nanoparticles of certain metals. Moskovits is a wholehearted supporter of plasmonic theory to explain the SERS effect. He argues that the alternative mechanisms proposed in the 1970s, chemical enhancement, has impeded the establishment of a universally accepted understanding, and hindered the development of SERS. Meanwhile, practical researchers should deal with the surface chemistry that arises in a given experiment on a molecule-by-molecule basis. Because it is trapped, the electrons at the very edge of the surface become excited and form what is defined as a surface plasmon. The intensity of Raman scattered radiation is proportional to the square of the magnitude of any electric fields acting on the analyte. Because of its proximity, any electric field from the particle will make a large contribution to the overall field. Under normal Raman scattering, the strength of the electromagnetic field suffers from the fact that the laser source is relatively far away, but the roughed-up surface enhances the electric field which delivers a boost to the intensity of the output signal. This plasmon or secondary electric field is the key to SERS for practical use in many areas of chemical analysis. Materials scientists have focused for years on developing the most efficient surfaces to exploit this beneficial plasmon effect. Ingenious

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techniques to create substrates now exist with the major goal to design discrete handheld Raman devices to detect concentrations down to single molecules for use in a vast range of applications from medical diagnostics and food safety to environmental monitoring and security. Nano revolution Because Sers is a nanoscale phenomenon rapid advances in nanotechnology have accelerated research over the last decade. The availability of near-field microscopes and scanning tunnelling microscopy and spectroscopy has led to the creation of an entire industry dedicated to making small, cheap Raman devices. There are many molecules of interest that do not adsorb spontaneously on silver and gold surfaces. Gold and silver have always been at the heart of Sers because they have a full d orbital of electrons and a single s electron. That does not mean there are no other options so Moskovits and Van Duyne and most others in the field believe it is essential to design new substrates and molecular capture strategies using nanotechnology. Research and trials have been carried out on partition layers similar to HPLC supports, transition metal overlayers, covalent capture ligands, metal organic frameworks and aptamers. Sensing the future Last summer, Shekhar Sharma and a team at the Agri Food and Biosciences Institute in Belfast, Northern Ireland, announced the results of tests on a new substrate based on nanostructures and using copper. They used measured volumes of the model dye rhodamine 6G dried onto a substrate consisting of a copper surface on which metallic silver in the form of nanostructures and dendritic accumulations had been deposited. His results showed that Sers was able to detect the dye down to a concentration of 0. If we can tune a substrate to any excitation wavelength, the game will change This new substrate was tested for its ability to detect both melamine , a potential food contaminant , and glyphosate , an organophosphate herbicide. The group detected melamine down to a level of 0. The Sers technique enhancement factor was determined and averaged at about over conventional Raman spectroscopy. At the heart of Sers substrate research is a universal substrate with a possible use over a broad range of excitation wavelengths. It might be possible using chip technology in which the chip has either a gradient of spheres or sub-chips with an array of sphere sizes to achieve some kind of universality. This is excellent for sensing trace molecules in security and defense. It can localise electromagnetic fields at the edges of surface nanopatterns and generate hot spots over a wide-range of excitation wavelengths. This unique feature has been validated using Sers sensing experiments which are sensitive to the localised field intensity applications. Space probes and particle accelerators will no doubt continue to attract rave reviews and make headline news round the world. Meanwhile humble chemists, delving into the mysteries of inner space, continue quietly on their Sers odyssey to a deeper understanding of the molecular world.