**Chapter 4**

Assembly of Nanoparticles for Plasmonics and Photonics

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Surface Enhanced Raman Spectroscopy (SERS) is a Raman Spectroscopic (RS) technique that provides greatly enhanced Raman signal from Raman-active analyte molecules that have been adsorbed onto certain speciallyprepared metal surfaces. Increases in the intensity of Raman signal have been regularly observed on the order of, and can be as high as and for some systems. The importance of SERS is that it is both surface selective and highly sensitive where as RS is neither. RS is ineffective for surface studies because the photons of the incident laser light simply propagate through the bulk and the signal from the bulk overwhelms any Raman signal from the analytes at the surface. SERS selectivity of surface signal results from the presence of surface

enhancement (SE) mechanisms only at the surface. Thus, the surface signal overwhelms the bulk signal, making bulk subtraction unnecessary.

There are two primary mechanisms of enhancement described in the literature: an electromagnetic and a chemical enhancement. The electromagnetic effect is dominant, the chemical effect contributing enhancement only on the order of an order or two of magnitude.

The electromagnetic enhancement (EME) is dependent on the presence of the metal surface’s roughness features, while the chemical enhancement (CE) involves changes to the adsorbate electronic states due to chemisorption of the analyte. The structural and molecular identification power of RS can be used for numerous interfacial systems, including electrochemical, modeled and actual biological systems, catalytic, in-situ and ambient analyses and other adsorbate-surface interactions. Due to the sensitivity of SERS, detection of trace molecules can be accomplished, as well. SERS is observed primarily for analytes adsorbed onto coinage (Au, Ag, Cu) or alkali (Li, Na, K) metal

surfaces, with the excitation wavelength near or in the visible region.

Theoretically, any metal would be capable of exhibiting SE, but the coinage and alkali metals satisfy calculable requirements and provide the strongest enhancement. Metals such as Pd or Pt exhibit enhancements of about for excitation in the near

ultraviolet.

The importance of SERS is that the surface selectivity and sensitivity extends RS utility to a wide variety of interfacial systems previously inaccessible to RS because RS was not surface sensitive. These include in-situ and ambient analysis of electrochemical, catalytic, biological, and organic systems. Zhou, et al discuss the alternative surface techniques (Sum Frequency Generation, Infrared Reflection Absorption Spectroscopy, and

Electron Energy Loss Spectroscopy) whose limitations include a need for ultra high vacuum (UHV) conditions, low wavenumber range, low sensitivity, and bulk phase interference. SERS can be conducted under ambient conditions, has a broader wavenumber range, is quite sensitive and is surface selective.

Reference:

1. Yue Zhuo, Huan Hu, Weili Chen, Meng Lu, Limei Tian, Hojeong Yu, Kenneth D. Long et al. "Single nanoparticle detection using photonic crystal enhanced microscopy." Analyst 139, no. 5 (2014): 1007-1015.
2. Jung-Hoon Park, Chunghyun Park, HyeonSeung Yu, Jimin Park, Seungyong Han, Jonghwa Shin, Seung Hwan Ko, Ki Tae Nam, Yong-Hoon Cho, and YongKeun Park. "Subwavelength light focusing using random nanoparticles."Nature photonics 7, no. 6 (2013): 454-458.
3. Prakash Nallathamby, Kerry J. Lee, and Xiao-Hong Nancy Xu. "Design of stable and uniform single nanoparticle photonics for in vivo dynamics imaging of nanoenvironments of zebrafish embryonic fluids." Acs Nano 2, no. 7 (2008): 1371-1380.
4. Xiaozhu Zhou, Yu Zhou, Jessie C. Ku, Chuan Zhang, and Chad A. Mirkin. "Capillary force-driven, large-area alignment of multi-segmented nanowires."ACS nano 8, no. 2 (2014): 1511-1516.
5. Xiaozhu Zhou, Yu Zhou, Jessie C. Ku, Chuan Zhang, and Chad A. Mirkin. "Capillary force-driven, large-area alignment of multi-segmented nanowires."ACS nano 8, no. 2 (2014): 1511-1516.
6. Daniel J. Park, Chuan Zhang, Jessie C. Ku, Yu Zhou, George C. Schatz, and Chad A. Mirkin. "Plasmonic photonic crystals realized through DNA-programmable assembly." Proceedings of the National Academy of Sciences112, no. 4 (2015): 977-981.
7. Daniel J. Park, Chuan Zhang, Jessie C. Ku, Yu Zhou, George C. Schatz, and Chad A. Mirkin. "Plasmonic photonic crystals realized through DNA-programmable assembly." Proceedings of the National Academy of Sciences 112, no. 4 (2015): 977-981.
8. Yu Zhou, Xiaozhu Zhou, Daniel J. Park, Korosh Torabi, Keith A. Brown, Matthew R. Jones, Chuan Zhang, George C. Schatz, and Chad A. Mirkin. "Shape-Selective Deposition and Assembly of Anisotropic Nanoparticles." Nano letters 14, no. 4 (2014): 2157-2161.
9. Yu Zhou, Xiaozhu Zhou, Daniel J. Park, Korosh Torabi, Keith A. Brown, Matthew R. Jones, Chuan Zhang, George C. Schatz, and Chad A. Mirkin. "Shape-Selective Deposition and Assembly of Anisotropic Nanoparticles." Nano letters 14, no. 4 (2014): 2157-2161.
10. Qing-Yuan Lin, Zhongyang Li, Keith A. Brown, Matthew N. O'Brien, Michael B. Ross, Yu Zhou, Serkan Butun et al. "Strong Coupling between Plasmonic Gap Modes and Photonic Lattice Modes in DNA-Assembled Gold Nanocube Arrays."Nano Letters 15, no. 7 (2015): 4699-4703.