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VIEW & PERSPECTIVE

Surface-enhanced Raman scattering beyond plasmonics

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In 1974, Fleischmann *et al.* found an unexpectedly enhanced Raman signal on the surface of roughened silver electrode, and attributed the signal enhancement to an increased surface area [1]. Three years later, Van Duyne *et al.* proved that the significantly strong Raman signals come from the surface enhanced efficiency, and discovered surface-enhanced Raman spectroscopy (SERS) [2]. Subsequently, collective oscillations of the electrons on nanostructured metals under the optical excitation are clearly defined as the fundamental of SERS [3]. After several decades of its first observation, SERS has enjoyed steady growth of interest in the research community, and it has become a commonly used and ultrasensitive sensing technique, in which the inelastic light scattering of molecules, as the unique molecular vibrational fingerprints, can be enhanced by one million times. And by placing the molecules within a nanogap between two plasmonic metal nanoparticles, the single molecule SERS can even be allowed, which benefits enormously from the enhancement of localized electromagnetic field [4, 5]. Recently, great efforts have been made to design and construct novel SERS-active substrates to enable multiple choices to fulfill the requirements of the practical applications of SERS and explore its potential in SERS applications in a wide variety of fields. Except for plasmonic noble metal materials (such as Au or Ag) which enhance Raman signals via the surface plasmon resonance, plasmon-free SERS active nanomaterials, for example transition metals, metal oxides and semiconductors, have undergone extensive development [6, 7]. Benefiting from the advantages of potentially low-cost material preparation, outstanding biomolecular compatibility, selectivity and recyclability, plasmon-free SERS active nanomaterials are ideal SERS substrates for use in the biomedical diagnosis, organic pollutants sensing, biochemical reactions monitoring. Compared with plasmon-based SERS, plasmon-free SERS, as an emerging frontier, owns diverse surface physical and chemical properties and inferior detection sensitivity. Therefore, intrinsic nature and enhancement mechanisms of plasmon-free SERS need to be rethought, and the detection sensitivity of plasmon-free SERS needs to be further improved to meet the demands of fundamental research and applications. Recently, Prof. Teng Qiu, who engaged in the application research of surface plasmon, and the collaborators explored a series of plasmon-free SERS active nanomaterials, for example, defect-engineered two-dimensional transition metal dichalcogenides, amorphous tungsten oxide films, $W_{18}O_{49}$/monolayer MoS_2 heterojunction, transition metal oxide chips, etc. [8–12]. These works not only promote the revealing of the inherent properties of plasma-free SERS, but also provide new ideas for the preparation and application of the plasmon-free substrates with high SERS activity. In Ref. [13], Qiu and the collaborators systematically reviewed the origin of ultrasensitive plasmon-free SERS. In this review, the background and the advantages of plasmon-free SERS are introduced. Then the roles of Mie resonance, charge transfer resonance, exciton resonance and molecular resonance in SERS based on plasmon-free substrates are discussed systematically. Moreover, enhancement strategies that used to improve the sensitivity of plasmon-free SERS and the application and future trend of plasmon-free SERS are summarized. This review not only includes basic understanding and state-of-the-art concepts, but also predicts what we can expect during the coming years in terms of the development of plasmon-free SERS. It can not only guide and motivate the currently active researchers in SERS, but also help to inspire a younger generation of scientists from different disciplines who can get excited about SERS and its emerging branches.

References

1. M. Fleischmann, P. J. Hendra, and A. J. Mcquillan, Raman spectra of pyridine adsorbed at silver electrode, *Chem. Phys. Lett.* 26(2), 163 (1974)
2. D. L. Jeanmaire and R. P. Van Duyne, Surface Raman spectroelectrochemistry (Part I): Heterocyclic, aromatic, and aliphatic amines adsorbed on the anodized silver electrode, *J. Electroanal. Chem.* 84(1), 1 (1977)
3. M. Moskovits, Surface roughness and the enhanced intensity of Raman scattering by molecules adsorbed on metals, *J. Chem. Phys.* 69(9), 4159 (1978)
4. H. Xu, E. J. Bjerneld, M. Käll, and L. Börjesson, Spectroscopy of single hemoglobin molecules by surface enhanced Raman scattering, *Phys. Rev. Lett.* 83(21), 4357 (1999)
5. K. Kneipp, H. Kneipp, I. Itzkan, R. R. Dasari, and M. S. Feld, Surface-enhanced non-linear Raman scattering at the single molecule level, *Chem. Phys.* 247(1), 155 (1999)

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6. Z. Q. Tian, B. Ren, and D. Y. Wu, Surface-enhanced Raman scattering: From noble to transition metals and from rough surfaces to ordered nanostructures, *J. Phys. Chem. B* 106(37), 9463 (2002)
7. J. Langer, D. Jimenez de Aberasturi, J. Aizpurua, R. A. Alvarez-Puebla, B. Auguié, et al., Present and future of surface enhanced Raman scattering, *ACS Nano* 14(1), 28 (2020)
8. X. C. Fan, M. Z. Li, Q. Hao, M. S. Zhu, X. Y. Hou, H. Huang, L. B. Ma, O. G. Schmidt, and T. Qiu, High SERS sensitivity enabled by synergistically enhanced photo induced charge transfer in amorphous nonstoichiometric semiconducting films, *Adv. Mater. Interfaces* 6(19), 1901133 (2019)
9. M. Z. Li, X. C. Fan, Y. M. Gao, and T. Qiu, $W_{18}O_{49}$/monolayer MoS_2 heterojunction-enhanced Raman scattering, *J. Phys. Chem. Lett.* 10(14), 4038 (2019)
10. X. Y. Hou, X. Y. Zhang, Q. W. Ma, X. Tang, Q. Hao, Y. C. Cheng, and T. Qiu, Alloy engineering in few layer manganese phosphorus trichalcogenides for surface enhanced Raman scattering, *Adv. Funct. Mater.* 30(12), 1910171 (2020)
11. X. Y. Hou, X. C. Fan, P. H. Wei, and T. Qiu, Planar transition metal oxides SERS chips: A general strategy, *J. Mater. Chem. C* 7(36), 11134 (2019)
12. X. Y. Hou, Q. Lin, Y. J. Wei, Q. Hao, Z. H. Ni, and T. Qiu, Surface-enhanced Raman scattering monitoring of oxidation states in defect-engineered two-dimensional transition metal dichalcogenides, *J. Phys. Chem. Lett.* 11(19), 7981 (2020)
13. L. Lan, Y. Gao, X. Fan, M. Li, Q. Hao, and T. Qiu, The origin of ultrasensitive SERS sensing beyond plasmonics, *Front. Phys.* 16(4), 43300 (2021)