

Nanostrukturali Metall Sirtlarda Raman Signaling Kuchayishi

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Annotatsiya: Bugungi kunda moddalarning spektroskopik va analitik tahlillarida Raman spektroskopiyasi keng qo'llanilib kelmoqda. So'nggi yillarda rivojlanib borayotgan nanostrukturali metall yuzalarda adsorbsiyalangan molekullarda Raman sochilishining kuchayishidan olingan natijalar muhim va yuqori amaliy ahamiyatga ega ma'lumotlar beradi. Ushbu maqolada SKRSning yuzaga kelish tarixi, Raman signalingning kuchayish mexanizmini tushuntirishga va uning imkoniyatlarini turli sohalarda yuqori darajada sezgir ilovalarning har xil turlarida qo'llash imkoniyatlarini ko'rsatib berildi.

Kalit so'zlar: Raman sochilishi, SKRS, MOP, kuchayish faktori, RRS.

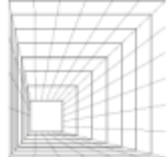
Raman Signal Enhancement On Nanostructured Metal Surfaces

Annotation: Today, Raman spectroscopy is widely used in spectroscopic and analytical analysis of substances. The results obtained from the enhancement of Raman scattering of molecules adsorbed on nanostructured metal surfaces, which have been developed in recent years, provide important and highly practical information. The history of the emergence of SERS, this article explains the mechanism of Raman signal amplification and shows its potential in various types of highly sensitive applications in various fields.

Key words: Raman scattering, SERS, MOF, enhancement factor, RRS.

Kirish

Sirtida kuchaytirilgan Raman spektroskopiyasi (SKRS) molekulyar spektral tahlillarning bir turi bo'lib, unda chastota o'zgarishi xususiy molekulyar tebranishlar bilan bog'liq va eng yuqori intensivlik molekulyar konsentratsiyaga mutanosibdir [1]. SKRS kashfiyotini 1974 yilda Fleischmann va uning jamoasi kumush elektrodning notekis yuzasida adsorbsiyalangan piridin molekullari Raman sochilish komponentalariga yaxshi ta'sir ko'rsatishi mumkinligini aniqladilar. Biroq, ular Raman signalingning kuchayishi metall elektrodning o'ziga xos sirt maydonining oshishi bilan bog'liq deb hisoblashadi [2]. Keyinchalik, 1977 yilda Janmari va Albrecht ham bu hodisani mustaqil ravishda kuzatdilar. Ular eksperimental ravishda Raman signalingning kuchayishi taxminan besh-olti darajaga teng ekanligini hisoblashdi va Raman signalini faqat katta o'ziga xos sirt maydoni bilan oshirish



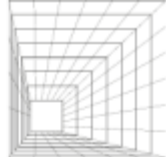
mumkin emasligini ta'kidlashdi. Ular bu hodisani plazma qo'zg'atuvchi rezonansli Raman effekti, ya'ni sirtida kuchayuvchi Raman sochilishi (SKRS) effekti tufayli yuzaga kelgan, deb taklif qilishdi [3,4]. Bugungi kunda SKRS sifat va miqdoriy tahlillarda yuqori sezuvchanlik, aniqlik va tezlik [5] xususiyatlaridan foydalangan holda, SKRS zararli moddalarni aniqlash [6], atrof-muhit tahlili [7], san'at asarlarini baholash [8], farmatsevtik tahlil, biomolekulyar identifikatsiya [9] va boshqa sohalarda keng qo'llanilib kelmoqda.

Adabiyotlar Tahlili

SKRS ta'sirini kuchaytirishning aniq mexanizmi adabiyotlarda hali ham munozarali masala bo'lib kelmoqda [10]. Bunda ikkita asosiy nazariya mavjud va ularning mexanizmlari sezilarli darajada farq qilsa-da, ularni eksperimental ravishda ajratish oson emas. Elektromagnit nazariya lokallashgan sirt plazmonlarining qo'zg'atilishini taklif qiladi, kimyoviy nazariya esa zaryad o'tkazuvchi komplekslarning shakllanishini taklif qiladi. Kimyoviy nazariya rezonans Raman spektroskopiyasiga asoslanadi. Rezonansli Raman spektroskopiyasi (RR spektroskopiyasi) - Raman spektroskopik tahlil usullaridan biri bo'lib, unda tushgan foton energiyasi energiya jihatidan tekshirilayotgan birikma yoki materialning elektron o'tishiga yaqin bo'ladi. Chastotaning mos kelishi (yoki rezonans) Raman sochilishining sezilarli darajada kuchayishiga olib kelishi mumkin, bu esa past konsentratsiyalarda mavjud bo'lgan kimyoviy birikmalarni o'rganishni osonlashtiradi. 2015 yilda SLIPSERS (Slippery Liquid-Infused Poous SERS) [12] deb nomlangan SKRS texnikasining yanada rivojlantirish bo'yicha olib borilgan tadqiqotlar elektromagnit nazariyani yanada qo'llab-quvvatladi [13].

Elektromagnit kuchayish lokal sirt plazmon rezonansi (LSPR) bilan bog'liq bo'lib, u fazoda metall yuza va erkin fotonlarning ta'sirlashuvi bilan yuzaga keladi va 10^4 - 10^{14} marta kuchaygan Raman signalini beradi. Muayyan sirtlarda adsorbatlar uchun Raman signalining intensivligining oshishi sirt tomonidan ta'minlangan elektr maydonining kuchayishi tufayli yuzaga keladi. Tajribada tushayotgan yorug'lik sirtga tushganda, lokalizatsiya qilingan sirt plazmonlari qo'zg'aladi. Plazmon (Plazmon - plazma tebranish kvanti) chastotasi ω_p nurlanish bilan rezonans bo'lganda maydon kuchayishi eng katta bo'ladi ($\omega = \omega_p/\sqrt{3}$ sferik zarralar uchun). Sochilish sodir bo'lishi uchun plazmon tebranishlari sirtga perpendikulyar bo'lishi kerak; agar ular sirt bilan bir tekislikda bo'lsa, hech qanday sochilish sodir bo'lmaydi [8-13]. Aynan shu talab tufayli, notekis yuzalar yoki nanozarrachalarning tuzilishi odatda SKRS tajribalarida qo'llaniladi, chunki bu yuzalar ushbu lokalizatsiya qilingan kollektiv tebranishlar yuzaga kelishi mumkin bo'lgan maydonni ta'minlaydi [14]. SKRS kuchayishi hatto uyg'ongan molekula metall nanozarrachalar joylashgan sirtidan nisbatan uzoqda bo'lganda ham yuz berishi mumkin, bu esa sirtida plazmonik hodisalarni yuzaga kelishini ta'minlaydi [15].

Sirtga tushadigan yorug'lik sirtidagi turli hodisalarni qo'zg'atishi mumkin, ammo bunday holatning murakkabligi yorug'lik to'lqin uzunligidan ancha kichik bo'lgan sirtlar tomonidan minimallashtirilishi mumkin, chunki tizim faqat dipolyar hissani aniqlashga asoslangan. Dipolyar kattalik plazmon tebranishlariga hissa qo'shadi, bu esa signal kuchayishiga olib keladi. SKRS effekti shunchalik aniqki, bunda maydon kuchayishi ikki marta sodir bo'ladi. Birinchidan, maydonni kuchayishi tushayotgan yorug'likning intensivligini



oshiradi, bu o'rganilayotgan molekulaning Raman tebranish rejimlarini qo'zg'atadi, shuning uchun Raman sochilish signali ortadi. Raman signali keyin tushayotgan yorug'likni qo'zg'atgan bir xil mexanizm tufayli sirt tomonidan yanada oshiriladi, natijada umumiy chiqish ko'proq ortadi. Har bir bosqichda elektr maydoni E^2 ga kuchayadi, bu jami E^4 ga kuchayishini beradi [16].

Kuchaytirish barcha chastotalar uchun bir xil emas. Raman signali tushayotgan yorug'likdan ozgina o'zgargan chastotalar uchun lazer nuri ham, Raman signali ham plazmon chastotasi bilan rezonansga yaqin bo'lishi mumkin va bu E^4 ga kuchayishga olib keladi. Chastota siljishi katta bo'lsa, tushayotgan yorug'lik va Raman signali ikkalasi ham ω_p bilan rezonansda bo'lolmaydi, shuning uchun ikkala bosqichda ham yaxshilanish maksimal bo'lmaydi [17].

Sirt materialini tanlash ham plazmon rezonans chastotasi bilan belgilanadi. Raman rejimlarini uyg'otish uchun ko'rinadigan va yaqin-infracizil nurlanish (NIR) ishlatiladi. Kumush va oltin SKRS eksperimentlari uchun odatiy metallardir, chunki ularning plazmon rezonans chastotalari ushbu to'lqin uzunligi diapazoniga to'g'ri keladi va ko'rinadigan va yaqin-infracizil nurlarining maksimal yaxshilanishini ta'minlaydi. Misning yutilish spektri ham SKRS tajribalari uchun maqbul diapazonga to'g'ri keladi [18].

Rezonans Raman spektroskopiyasi (RRS) orqali Raman sochilish intensivligining yuqori kuchayishini tushuntirish mumkin. Molekulyar va intermolekulyar zaryad o'tkazmalari Raman spektrining piklarini sezilarli darajada oshiradi. Xususan, sirtida adsorbsion xususiyati yuqori metall turlarida yuqori intensivlikdagi zaryad o'tishi tufayli metall yuzasida adsorbsiyalanuvchi turlar uchun kuchayish juda katta [19]. Ushbu rezonansli Raman kuchayishida ko'p tarmoqli bo'shliqlari bo'lgan kichik nanostrukturalardagi turlar SKRS uchun dominant hisoblanadi, chunki sirt plazmoni faqat nolga yaqin bo'shliqqa ega bo'lgan metall yuzasida hosil bo'ladi. Bu kimyoviy mexanizm, ehtimol, metall yuzasi uchun elektromagnit mexanizm bilan uyg'unlikda sodir bo'ladi [20].

Natijalar Va Muhokamalar

O'tkir uchlari, tor bo'shliqlari va agregatlari bo'lgan plazmonik nanostrukturalar, odatda, Raman sochilish signalini kuchaytiradi va ularning lokalizatsiyalangan sirt plazmon rezonansi (LSPR) to'lqin uzunligi, bir qancha faktorlarni o'zgartirish orqali masalan, nanozarracha tarkibi, o'lchami, qotishma nisbati va boshqalar bilan o'zgartirilishi mumkin [21].

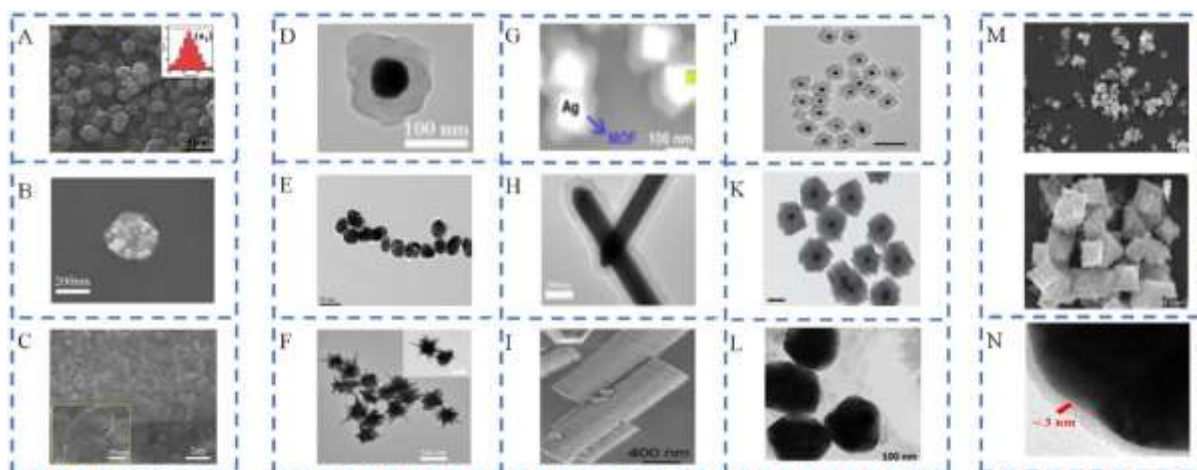
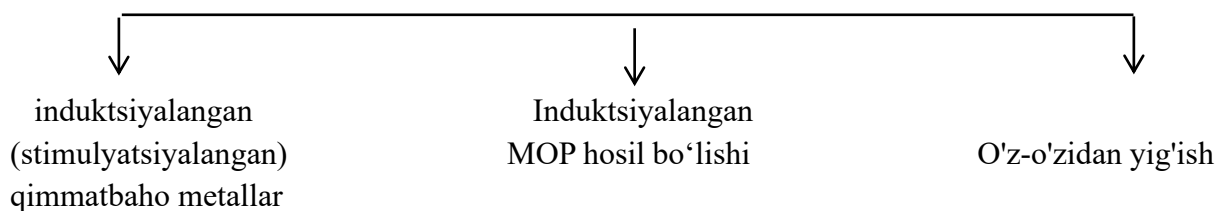
SKRS da kimyoviy kuchayish metall qatlam va metall substrat yuzasida absorbsiyalangan namuna o'rtasida zaryad o'tishi natijasida yuzaga keladi [15]. Ko'pgina kimyoviy kuchayish jarayonlari quyidagilarni o'z ichiga oladi: (i) jarayonda ishtirok etuvchi molekular qutblanishining kuchayishi, (ii) uyg'otuvchi foton bilan uyg'otilgan molekulyar elektron qo'zg'alish yoki (iii) elektron qo'zg'alishda ishtirok etuvchi orbitallar tizimning turli qismlarida lokalizatsiya qilingan (zaryad o'tishlariga mos keladigan), ya'ni dastlab metall orbitalda joylashgan elektron organik molekulada lokalizatsiya qilingan molekulyar orbitalga ko'tarilgan maxsus holat [14]. Ba'zi maxsus sistemalarda kimyoviy kuchayish SKRS effektiga sezilarli hissa qo'shishi mumkin [16]. Shunday qilib, ko'plab tadqiqotchilar tomonidan dastur



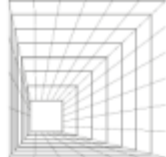
talablarini bajarish uchun samarali SKRS substratlar o'rganib chiqilgan. Mavjud materiallar bilan solishtirganda, asl metallar (oltin, platina va boshqa platina guruhi metallari - ruteniy, rodiy, palladiy, osmiy, iridiy) bilan integratsiyalashgan holda hosil qilingan kompozit materiallar yuqori samaraga ega SKRSni takomillashtirishni amalga oshirishda o'ziga xos afzalliklarga ega, chunki kompozit materiallar tanlab olish, shuningdek, tez singdirish va signalni kuchaytirish xususiyatiga ega bo'lishi mumkin [21,22]. Metall-organik panjaralar (MOP) asosidagi SKRS kompozit substratlari SKRS qo'llanilishida yuqoridagi afzalliklarga ega tadqiqotlarni amalga oshirish uchun samarali alternativ ekanligi ko'rsatildi.

Odatda, an'anaviy SKRS substratlarini ikkita asosiy toifasiga bo'lish mumkin: asl metall substrat va yarim o'tkazgich substrat. Metall substratlar, ayniqsa Au, Ag va Cu kabi qimmatbaho metallar kuchli plazma birikmasini keltirishi mumkin, bu esa asosan elektromagnit kuchayish mexanizm mavjudligi sababli SKRS signalining kuchayishiga olib keladi. Bundan farqli o'laroq, kimyoviy mexanizmning mavjudligi sababli, $W_{18}O_{49}$, Cu_2O va MoS_2 kabi ba'zi yarimo'tkazgichli SKRS substratlari ham Raman signalini sezilarli darajada kuchayishini ko'rsatdi, bunda analitning yarimo'tkazgich chegarasida zaryad o'tkazish katta rol o'ynaydi. Hozirgi vaqtda MOP-SKRS substratlari asosan MOP va qimmatbaho metall nanozarrachalarining kombinatsiyasidan iborat.

SKRS substrati sifatida MOP bilan birlashtirilgan qimmatbaho metallar



1-rasm. (A–C) SERS substrati MOP ichki va tashqi yuzalarida ishlab chiqarish uchun qimmatbaho metall nanopartikullarni induksiya qilish orqali sintezlangan [23-25]. (D-F) Yadro sifatida oltin nanozarrachalar va qobiq sifatida MOP bo'lgan SKRS substrati [26-28]. (G-I) Yadro sifatida kumush nanozarrachalar va qobiq sifatida MOF bo'lgan SKRS substrati [30-32]. (M,N) MOP va Nobl Metal Nanozarrachalarining o'z-o'zidan yig'ilgan SKRS substratlari [57,58].

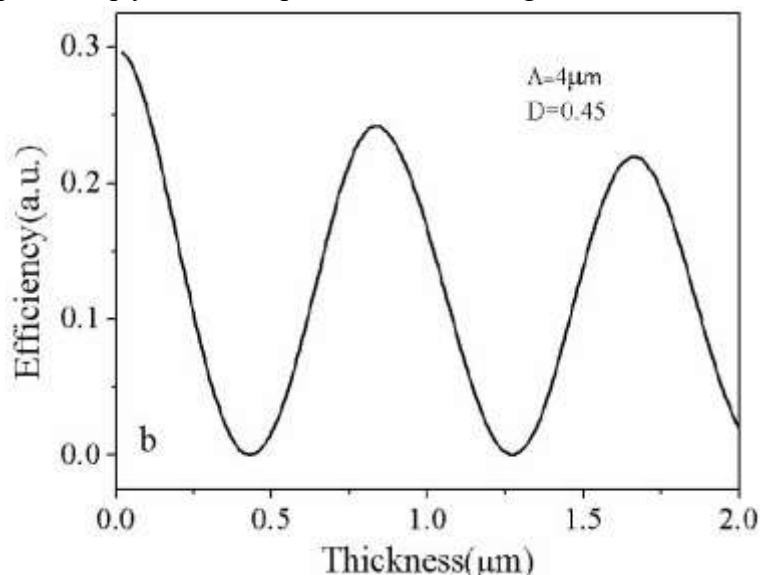


MOP va metall substratning kombinatsiyasi SKRS tahlilining samaradorligini sezilarli darajada oshiradigan sinergik effekt yaratadi. Metall-Organik panjaralarni (MOP) qimmatbaho metallar bilan birgalikda sirtida-kuchaygan Raman sochilish (SKRS) substratlari sifatida qo'llash asoslari 1-rasmda ko'rsatilganidek tavsiflanadi.

Kremniy panjarasida Raman signali kuchayishi

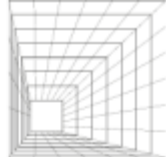
Sochilish va diffraksiyaning optik xususiyatlari yorug'lik to'lqini panjaraga ta'sir qilganda namoyon bo'ladi. Panjara fotonning sochilish yo'lini kengaytirishi mumkin. Shu bilan birga, akslangan yorug'lik to'lqini panjara yuzasiga interferensiya hodisasini keltirib chiqarishi mumkin, bu esa doimiy to'lqinni hosil qiladi va bu sekinlashgan yorug'lik effekti deb ataladi. Sekinlashgan yorug'lik effekti yutuvchi qatlamda yorug'lik tarqalish tezligini pasaytiradi va yorug'lik va muhit o'rtasidagi ta'sir vaqtini oshiradi. Qat'iy to'lqin tahlili (RCWA) [24] panjara maydoni va diffraksiya samaradorligini simulyatsiya qilish uchun ishlatilgan. tushish burchagi 5° ga teng. Yassi tekislik diffraksiyasi bilan solishtirganda, to'rtburchakli panjara ham elektr, ham magnit maydon komponentiga yaxshi lokal ta'sir ko'rsatadi. Bu umumiy sochilish samaradorligini oshirishi va Raman signalini kuchaytirishi mumkin. Raman sochilish intensivligi, shuningdek, qo'zg'atuvchi nurning kirib borish chuqurligiga bog'liq bo'lib, yorug'likning kirib borish chuqurligi 785 nm to'lqin uzunliklari uchun c-Si da taxminan $10 \mu\text{m}$ ni tashkil qiladi [26]. Biroq, 785 nm to'lqin uzunligi namunalar uchun yorug'lik kirib borish chuqurligining qiymati g'ovak chuqurligidan sezilarli darajada yuqori. Shunday qilib, 785 nm to'lqin uzunligida uyg'otilganda kremniy panjarada Raman sochilish intensivligining kuchayishi yorug'lik kirib borish chuqurligining spektral ta'siri bilan bog'liq emas.

Kremniy panjara ustidagi yorug'likning Raman sochilishini o'rganishda elektr maydonining ko'p marta qaytishi va taqsimlanishini hisobga olish kerak.



2-rasm. Akslantirish difraksiya samaradorligi panjara kanavkalari chuqurligiga qarab o'zgarib turadi (panjara davri 4 mkm, to'ldirish koeffitsienti 0,45, nolinchi tartib o'lchangan)

2-rasmda panjara g'ovagining qalinligiga qarab akslantirish diffraksiyasining samaradorligining o'zgarishini ko'rsatadi. Natijalar shuni ko'rsatadiki, panjara qalinligi 500 nm dan kam bo'lsa, akslantirish diffraksiyasining samaradorligi asta-sekin kamayadi.

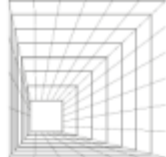


Xulosa

Sirtida kuchaytirilgan Raman spektroskopiyasi atamasi an'anaviy Raman spektroskopiyasiga o'xshash ma'lumotni shunchaki kuchaytirilgan signal bilan taqdim etishini anglatadi. Ko'pgina SKRS tajribalarining spektrlari sirtidan tashqari kengaytirilgan spektrlarga o'xshash bo'lsa-da, ko'pincha mavjud rejimlar sonida farqlar mavjud. Oddiy Raman spektrida topilmagan qo'shimcha rejimlar SKRS spektrida mavjud bo'lishi mumkin, boshqa rejimlar esa yo'qolishi mumkin. Har qanday spektroskopik tajribada kuzatilgan rejimlar molekularning simmetriyasi bilan belgilanadi va odatda Tanlash qoidalari bilan umumlashtiriladi. Molekulalar sirtga adsorbsiyalanganda, sistemaning simmetriyasi o'zgarishi, molekula simmetriyasini biroz o'zgartirishi mumkin, bu esa rejim tanlashda farqlarga olib kelishi mumkin. So'nggi yillarda MOPga asoslangan SKRS substratlari turli sohalarida samarali qo'llanilmoqda. Ushbu sharhda biz MOP ning SKRSdagi o'ziga xos roli, MOPga asoslangan SKRS substratlarini tasniflash va MOP-SKRS substratlarini atrof-muhit, biomeditsina, qishloq xo'jaligi va boshqalarda qo'llash mumkin.

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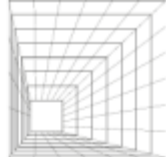
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