

Application of Silicon Nanoparticles-Based Sensors: Silicon-Based Surface Enhanced Raman Scattering, High Energy Material Sensing, Glucose Sensing Dopamine Sensing, Antibiotic and Biological Sensing

Ali Nassr Fadhil Al-Talla¹, SAJJAD HASAN ABBOD AL-RUBAYE², GHADEER KETAB YOUSIF AL-KHAFAJI³

^{1,2,3}Hillah University
College, Medical Devices
Engineering Technology,
Iraq

Abstract:

It is of special importance to design a ratiometric sensor using silicon nanoparticles. New research suggests that by modifying the size and surface modification groups of silicon nanoparticles, their fluorescence may be tuned across the whole visible spectrum. More accurate quantitative measurements with a better signal-to-noise ratio are possible with the dual emission technique that uses silicon nanoparticles. Building multi-detection systems is another use case. Also, by fine-tuning the reaction and fluorescence of silicon nanoparticles, one can accomplish such a multiple detection system. In these setups, we selectively mix several target analytes using silicon nanoparticles with various surface groups. Without the use of harmful metals, it is possible to detect numerous analytes simultaneously in this manner. The impact of surface groups on conductivity and fluorescence is one of several outstanding issues, despite the fact that silicon nanoparticle production and surface modification have come a long way. Although different surface functional groups can cause silicon nanoparticles to exhibit varied fluorescence, the specific process by which this occurs remains unclear. Similarly, there has been very little investigation into how different surface modification groups affect the electrical structure of silicon nanoparticles. We can tailor the silicon nanoparticles to the analysis object's reduction potential if we can determine the effect of surface groups on the band edge. To better build sensors using silicon nanoparticles, it is helpful to have a firm grasp of these fundamental characteristics. Also, we need to find ways to modify surfaces that work better. Because most functional modifications to the material's surface cannot reach every surface, there may be areas that are susceptible to oxidation. Many synthetic silicon nanoparticles will have their surface modification layers changed, rendering them unusable for future sensor manufacture; this will impede their commercial development and production. Silicon nanoparticles have a low quantum yield, which is a major drawback when compared to other semiconductor quantum dots. To enhance the quantum yield, we can refine the surface modification technique and link more surface ligands to enable the detection of more targeted analytes. Quantum dot fluorescence can be significantly impacted by the weak contact between surface ligands and analytical objects. Additional research and development is required to perfect the process of creating hybrid materials using silicon nanoparticles. Could we possibly create a more efficient FRET-based sensor by combining silicon nanoparticles with polymers, dyes, and carbon dots? Alternatively, in SERS sensors based on silicon nanohybrids, the increase of SERS is derived from the plasmon resonance interaction of metal nanoparticles and the effective plasmon resonance coupling between metal nanoparticles and adjacent silicon substrates. Secondly, the SERS signals are guaranteed by the closely defined plasmonic nanoparticles on the silicon wafer or silicon nanowires. To take advantage of these features, various silicon nanohybrids have been used to create SERS sensors that are high-quality, portable, inexpensive, sensitive enough, specific enough, reproducible, and capable of multiplexing detection. These hybrids can be decorated with graphene, gold, silver nanoparticles, silicon nanowires, or silicon wafer, among others. This laid the groundwork for the development of sensitive, selective, and multiplexed SERS sensing systems based on silicon, which allowed for the sensitive, molecular-to-cellular-level examination of a wide range of targets.

Corresponding Author:

Ali Nassr Fadhil Al-Talla[†],
Hillah University College,
Medical Devices
Engineering Technology,
Iraq

Keywords: Silicon Nanoparticles, Silicon-Based Surface, High Energy, Glucose Sensing Dopamine Sensing, Biological Sensing

Introduction

It is critical to create a quick, cheap, and on-site detection sensor system for explosives because of the severe risks they pose to human health, the environment, and the safety of those around them. Nitro aromatic chemicals have long been recognised for their ability to extinguish the fluorescence of silicon-based nanosystems, such as porous silicon and partially oxidised silica nanoparticles. Adding nitrobenzene (NB), dinitrotoluene (DNT), or trinitrotoluene (TNT) vapour to the surging air flow can quench the fluorescence of porous silicon, according to Professor Sailor's team's proof. Transferring electrons from nanocrystals in a porous silicon matrix to nitro aromatic compounds is the process that quenches them. Using this approach, the lowest detectable amounts of dinitrotoluene are 2 ppb and trinitrotoluene are 1 ppb. Researchers led by Germanenko found that nitro aromatic compounds with a reduction potential lower than that of the silicon nanoparticles themselves—for example, 3-minute 5-dinitrobenzonitrile, 1-minute 4-dinitrobenzene, 2-minute 4-dinitrotoluene—can stifle the fluorescence of certain silicon nanoparticles. These investigations laid the groundwork for subsequent investigations into the use of zero-dimensional silicon nanoparticles as a sensing system for the detection of explosives mostly composed of nitro aromatic chemicals. A further study by Veinot et al. detected nitroaromatic chemicals, nitrosamines, and nitrate esters by immobilising red dodecyl-modified silicon nanoparticles on paper sensors [1, 2]. A paper sensor with a detection limit of 18.2 ng for DNT is capable of immediately and quantitatively determining analytes. Using this method, the detection limit in the aqueous phase can reach 1 nM. The action of surface amino groups causes FRET, which in turn quenches the fluorescence. Additional nitro aromatic chemicals (e.g., NB and DNT) and charged metal ion interferers (e.g., Cu^{2+} , Ca^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Ag^{+} , Al^{3+} , Fe^{3+} , and Fe^{2+}) were detected using this sensing system, demonstrating that the impact of metal ion interference was negligible. Professor Nguyen's group then employs silicon nanoparticles for nitroaromatic chemical detection. Alkyl oligomers (red emission), alkyl monomers (red emission), and alkylamines (blue emission). Using the electron transfer quenching mechanism [3-5], they demonstrated that alkyl oligomers were less susceptible to gaseous nitro aromatic chemicals than alkyl monomers. It is worth noting that nitro-aromatic chemicals had less of an impact on the blue-emitting silicon nanoparticles with amino groups compared to the red-emitting alkyl particles and the blue-emitting silicon nanoparticles system that had been previously documented. Because the amino groups were connected to the surface of the silicon nanoparticles instead of at the end of the surface modification layer, which prevented the development of the Meisenheimer complex that is essential for enhancing the energy transfer effect of fluorescence resonance.

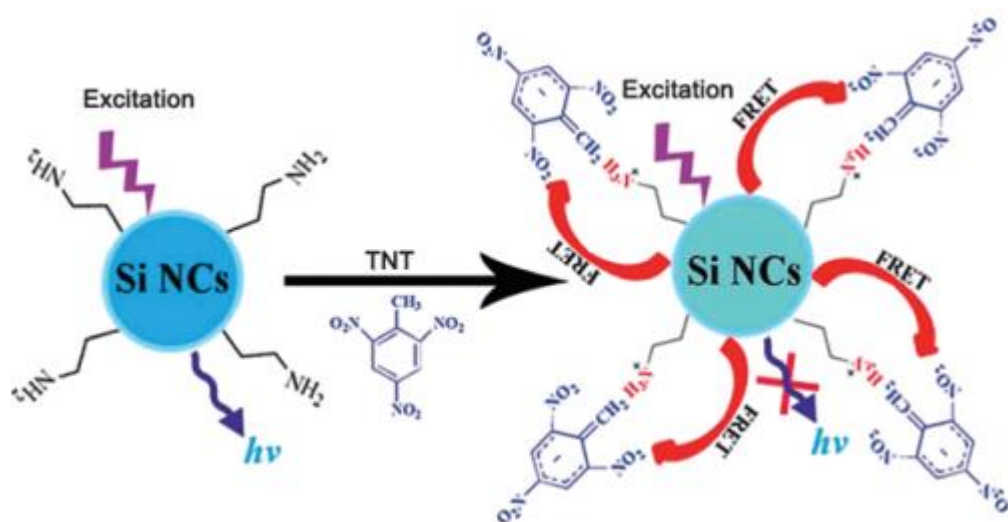


Figure 1. The mechanism of the fluorescence resonance energy transfer effect between the amino complex of TNT and silicon nanoparticles.

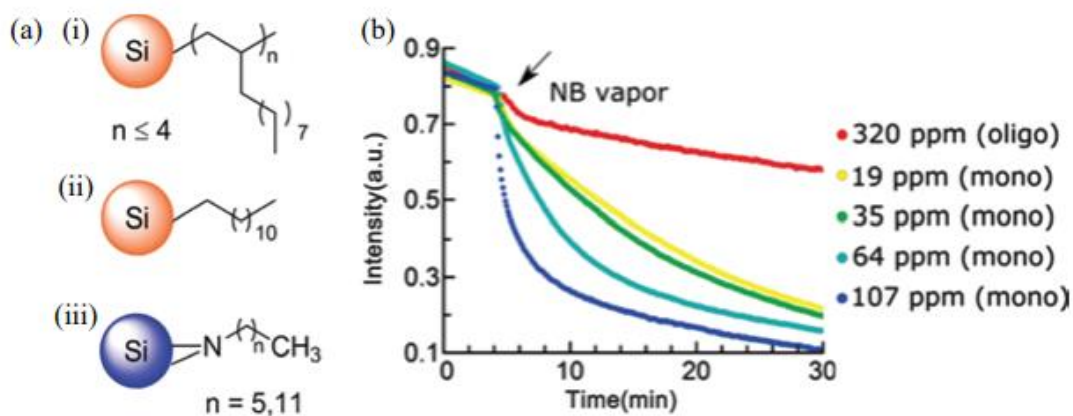


Figure 2. (a) The reaction of silicon nanoparticles with different surface groups of (i) alkyl oligomer, (ii) alkyl monomer, and (iii) alkylamine to nitroaromatic compounds. (b) The fluorescence changes of silicon nanoparticles functionalized by alkyl oligomers and dodecyl monomers on filter paper after reacting with different concentrations of nitrobenzene.

Ultra-High-Performance Material Feeling

Metal cation detection

U.S. officials have reiterated that metal cation detection is critical in light of the country's current water safety concerns.³⁹ So, a low-limit-of-detection method for trace metals that is also highly selective is required. It is impossible to overlook a difficulty, even though numerous papers have thoroughly examined quantum dots as optical sensors for metal ion detection. Is it practical and reasonable to utilise a metal sensor that is intrinsically poisonous, like cadmium telluride quantum dots, to detect harmful metals? There is some evidence that porous silicon nanoparticles can sense and detect metal ions; this is in line with their previous use as sensors for electrochemistry and energy conversion [6, 7]. One method for detecting mercury ions involves using blue-emitting silicon nanoparticles that have amino groups linked to them. The fluorescence will be brought back when the metal chelate is added again. Static and dynamic quenching are both components of the quenching mechanism. There have been reports that these silicon nanoparticles, which generate a blue light, are sensitive enough to detect Cu^{2+} and Cr^{4+} .

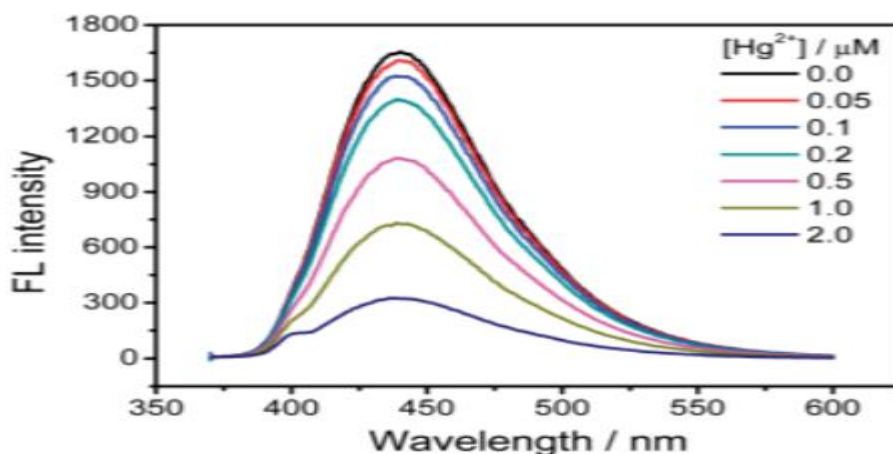


Figure 3. Effects of different concentrations of Hg^{2+} on the fluorescence of silicon nanoparticles.

Glycemic Monitoring

More than 15 million individuals across the globe are living with diabetes, which is why glucose testing is important.⁴⁶ A cheap, easy, and dependable way to monitor glucose needs to be developed. Porous silicon has many potential applications as a biosensor, including the detection of glucose and other analytical chemicals. In contrast,

research on silicon nanoparticles' potential uses in this area is scant. Yi and colleagues created a glucose oxidase (GOX) and phosphate buffer solution sensor by combining blue-glowing silicon nanoparticles with hydride groups on their surfaces.⁴⁹ In an outside setting, the system solution's fluorescence can be maintained for at least six hours [7-9]. Glucose oxidase in the silicon nanoparticle solution will oxidise and breakdown glucose when glucose is introduced, simultaneously producing gluconic acid and hydrogen peroxide. Contact between the surface of the silicon nanoparticles and the generated H₂O₂ transfers electrons from the conduction band of the nanoparticles to the reactive oxygen species, quenching the fluorescence of the nanoparticles and resulting in the production of H₂O and O₂. A complete cycle of electron transfer mediated by glucose oxidation will be formed when the extra oxygen that is produced returns to the catalytic activity of glucose oxidase. Under ideal circumstances, this sensor can detect glucose at a concentration as low as 0.68 mM. A number of amino acids, metal ions, and other glucose analogues were introduced for detection in order to examine the selectivity of this sensor. Findings demonstrate that these interferers have a negligible impact on the sensory system even when their concentration is 20 times higher than glucose. Another glucose sensor was created by Chen et al., which analyses colour proportions using the peroxidase-like activity of silicon nanoparticles. Additionally, they combined a solution containing glucose oxidase, 3-tetramethylbenzidine (TMB), and silicon nanoparticles that emitted blue light and had hydride groups linked to their surfaces.⁵⁰ In addition, they created a solution of glucose oxidase [10, 11], tetramethylbenzidine, and blue-emitting silicon nanoparticles that had hydride groups attached to their surfaces. Reactive oxygen species are formed when silica nanoparticles are broken down by glucose oxidase, which catalyses the oxidation of glucose to H₂O₂. Similar to how TMB can be oxidised by H₂O₂ in the presence of peroxidase, this chain reaction transforms silicon nanoparticles into electrophilic substances and causes them to oxidise TMB.

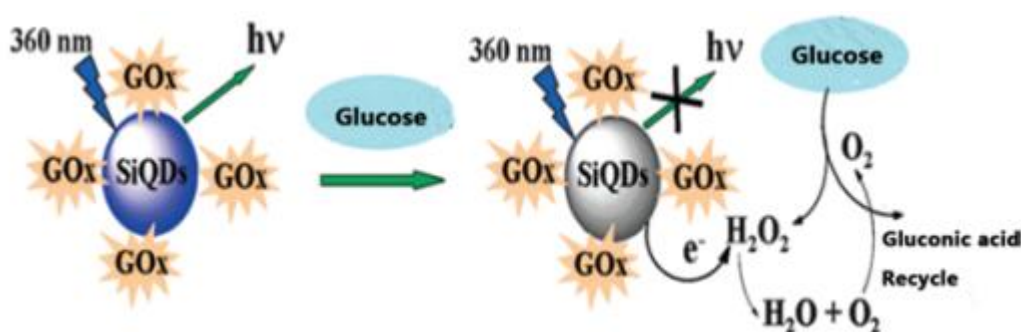


Figure 4. Graphical illustration of glucose sensor based on silicon nanoparticles.

Detecting Dopamine

An essential neurotransmitter, dopamine influences a wide variety of mental processes. It is crucial to detect and quantify dopamine in the body because metabolic diseases can result from excessive dopamine secretion and Parkinson's disease can be caused by insufficient dopamine secretion. Dopamine detection using fluorescent quantum dots has been attempted, but the sensitivity of these dots is insufficient for real-world use. By attaching amino groups to the surface of blue-emitting silicon nanoparticles [12-14], Zhang and colleagues were able to selectively detect dopamine. The fluorescence recovery was measured after three hours of shaking and mixing after adding dopamine solution to a solution of phosphate buffer and synthesised silicon nanoparticles. The findings demonstrated a direct correlation between dopamine concentration and the degree to which silicon nanoparticles quenched fluorescence. The detection limit of dopamine was as low as 0.3 nM, and it was remarkably unaffected by various interferers, including proteins, amino acids, peptides, and metal ions. This sensor device primarily uses the FRET effect to quench fluorescence. Excited silicon nanoparticles transfer their electrons to molecules of oxidised dopamine. Additionally, the scientists note that fluorescence quenching could be caused by the action of electron transfer between donor silicon nanoparticles and receptor dopamine.

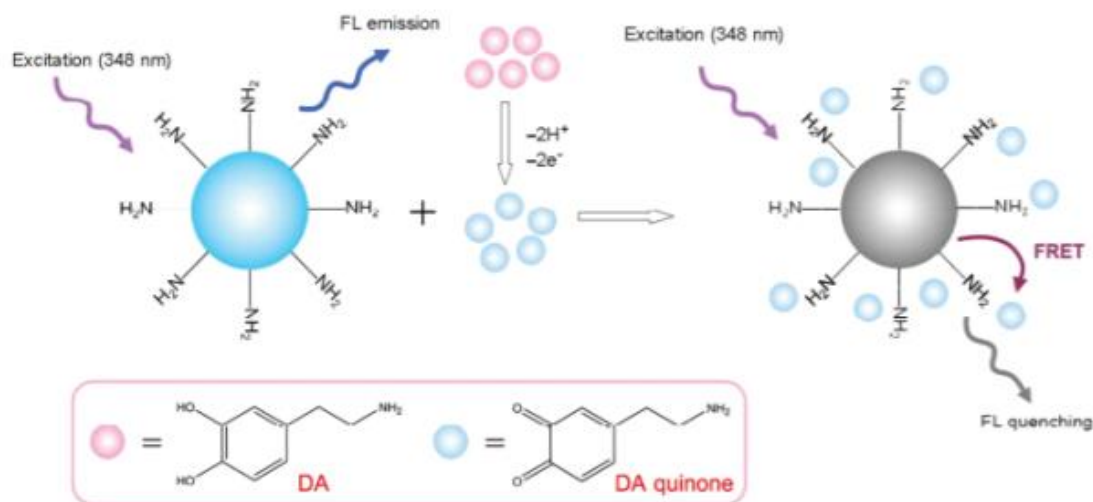


Figure 5. When dopamine is added to the system, the mechanism of fluorescence quenching of silicon nanoparticles is explained.

Recognising Gases

Modern industrial and residential production rely heavily on gas and steam detectors. The detection and analysis of lung gases, as well as the biological, chemical, and food industries, all place a premium on highly specific alcohol testing. Porous silicon has reportedly been developed as a sensor for detecting alcohol, according to several recent articles. Another method for detecting alcohol vapour is using silicon nanoparticles. Zhang and coworkers were able to detect ethanol by combining optical fibre dimensions with red-glowing silicon nanoparticles. We soak the optical fibre in a solution of amino-group-attached silicon nanoparticles for a while, and then we take it out to dry naturally [15, 16]. The silicon nanoparticles at the optical fiber's tip will cluster together into micron-sized particles as a result of this entire process. If we place this structure material in a dry stream of oxygen, water vapour, or ethanol vapour, we can observe the expected change in the fluorescence of silicon nanoparticles. With the optical fibre immersed in steam for 15 seconds, the technology is able to detect ethanol at concentrations as low as 380 parts per million .

Drug Sensitivity

Tetracycline is an antibiotic in the tetracycline family. It has broad medical and agricultural applications, including the treatment of bacterial infections and the addition of certain nutrients to food.^{60,61} Nevertheless, tetracycline resistance can develop from overuse,⁶² so it's crucial to monitor tetracycline levels in food. We should prioritise developing a quick, accurate, and selective detection method. Electrochemical impedance sensors that detect tetracycline have been developed using amino-functionalized silicon nanoparticles.⁶³ The blue fluorescence of surface-modified silicon nanoparticles [17-19] can be neutralised by tetracycline, chlortetracycline, and tetracycline, according to research by Lin and Wang.²⁹ Silicon nanoparticles' fluorescence was directly induced by the addition of tetracycline, oxytetracycline, or chlortetracycline to a phosphate buffer solution that already included the nanoparticles. As for tetracycline, oxytetracycline, and chlortetracycline, their respective detection limits are 25.9 nM, 20.4 nM, and 28.3 nM. It appears that a ground state complex is created during the reaction to quench the fluorescence of silicon nanoparticles, since the addition of tetracycline molecules has no influence on their fluorescence lifespan. It is thought by the researchers that the ground state complex is formed when the amino group on the surface of silicon nanoparticles combines with tetracycline molecules . Fluorescence quenching may also occur as a result of the spectrum overlap between the emission spectra of silicon nanoparticles and the absorption peaks of tetracycline molecules. Nevertheless, the degree to which the emission and absorption spectra overlap between the two is insufficient to generate the FRET effect [20, 21]. By detecting and analysing the milk samples with silicon nanoparticles, we were able to confirm the practical use of these tiny particles. The milk's proteins and lipids were

extracted and separated prior to the study. The luminosity of silicon nanoparticles was seen to be diminished following their incorporation into milk.

Sensing for Pesticides

The extensive use of pesticides in global agriculture results in long-term environmental harm and the buildup of residues in the ecosystem.⁶⁴ The majority of pesticides have carbamates and organophosphorus compounds, which are known to kill by suppressing respiratory chain function and destroying cholinases, which control the body's acetylcholinesterase levels.⁶⁶ A lot of the pesticide detection technologies are quite pricey, necessitating extensive sample pre-processing procedures, expensive equipment, and highly trained specialists. The use of heavy metal quantum dots raises safety concerns, despite the fact that fluorescent quantum dot sensing detection is a relatively simple detection technology [22-25]. The number of Another option for pesticide detection is the use of oxide-coated porous silicon sensors. Additionally, these investigations demonstrated the viability of using silicon nanoparticles for pesticide detection. The use of surface-modified silicon nanoparticles with blue light and hydride for pesticide detection has recently been validated.⁶⁷ The first step was to combine acetylcholine, phosphate buffer solution, acetylcholinesterase, and choline oxidase with silicon nanoparticles. After an interaction between acetylcholine and acetylcholinesterase, choline is formed. Choline oxidase subsequently interacts with this choline to make hydrogen peroxide. In order to stop the recombination of electron holes and turn off the fluorescence of silicon nanoparticles in solution, an active oxygen compound in H₂O₂ will grab the electrons from their conduction band. The final step in conducting fluorescence analysis was to add carbaryl, a carbamate insecticide, to the solution. After 15 minutes of reaction at 40°C in a dark setting, the results were recorded [26-27]. By reducing acetylcholinesterase activity, carbaryl prevents acetylcholinesterase from reacting with choline oxidase and, in turn, reduces H₂O₂ generation. Reducing the concentration of H₂O₂ in the solution causes a decrease in electron transfer from silicon nanoparticles to H₂O₂, leading to an increase in the fluorescence intensity of the nanoparticles. The min detection limit for carbamate pesticides, including parathion, diazinon, methamidophos, and carbamate, was found to be 7.25×10^{-9} , 3.25×10^{-8} , 76×10^{-8} , and 1.9×10^{-7} g/L, according to the researchers .

pH sensor for the environment and biology.

Materials with optical characteristics that respond to changes in pH have recently attracted a lot of interest from researchers in the environmental, medical, and biological domains. Although quantum dots have been modified to sense pH in numerous research, silicon nanoparticles have received less attention in this area. To create a pH sensor, Feng and colleagues utilised amino group-coated silicon nanoparticles that emitted a blue light. This allowed them to measure the pH of water samples. A Beretan-Robison buffer solution containing silicon nanoparticles was used, with a pH range of 2.01 to 11.02. Through the measurement of fluorescence at various pH values, it was discovered that the fluorescence intensity of silicon nanoparticles rose steadily as the pH in the solution increased, and stayed constant at pH 7. In a similar vein, they also recorded levels of potential compounds that could interfere, including K⁺, Cd²⁺, Mg²⁺, Ca²⁺, NO₃⁻, SO₄²⁻, and PO₄³⁻. The sensing mechanism of silicon nanoparticles is remarkably unaffected by them, it turns out. It is possible to use SiNPs sensors for intracellular pH monitoring in addition to ambient pH detection. Using living cells as an example, He et al. (2016) demonstrated the use of SiNPs sensors for both long-term and real-time intracellular pH (pHi) measurement. The addition of pH-sensitive dopamine molecules and pH-insensitive rhodamine B isothiocyanate (RBITC) molecules to silicon nanoparticles . Usually, the SiNPs sensors showed a broad pH response (around 4 to 10), a strong fluorescence signal (with a high photoluminescence quantum yield, or PLQY, of about 15% to 25%), great photo-stability (with only about 9% intensity loss after 40 minutes of continuous UV irradiation), and weak cytotoxicity (with cell viability of treated cells remaining above 95% during a 24-hour treatment) [28-31]. The created sensors are well-suited for the ratiometric monitoring of changes in pHi over long periods of time and in real-time because of their exceptional properties.

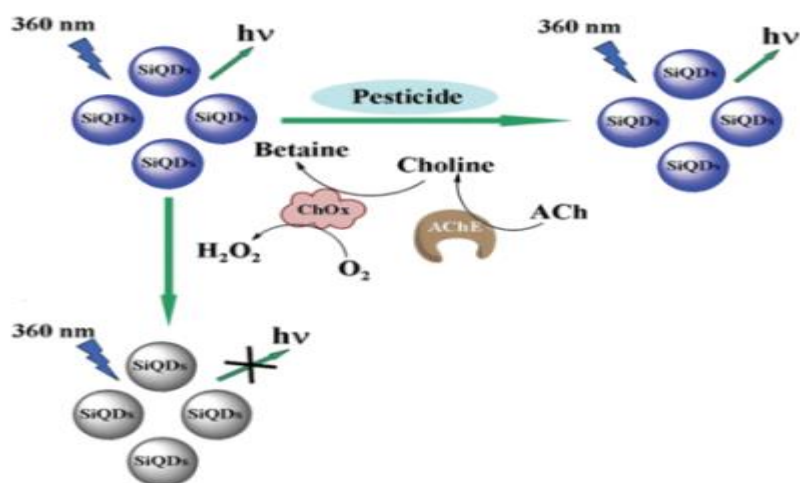


Figure 6. Sensing mechanism of silicon nanoparticles sensor based on pesticide detection.

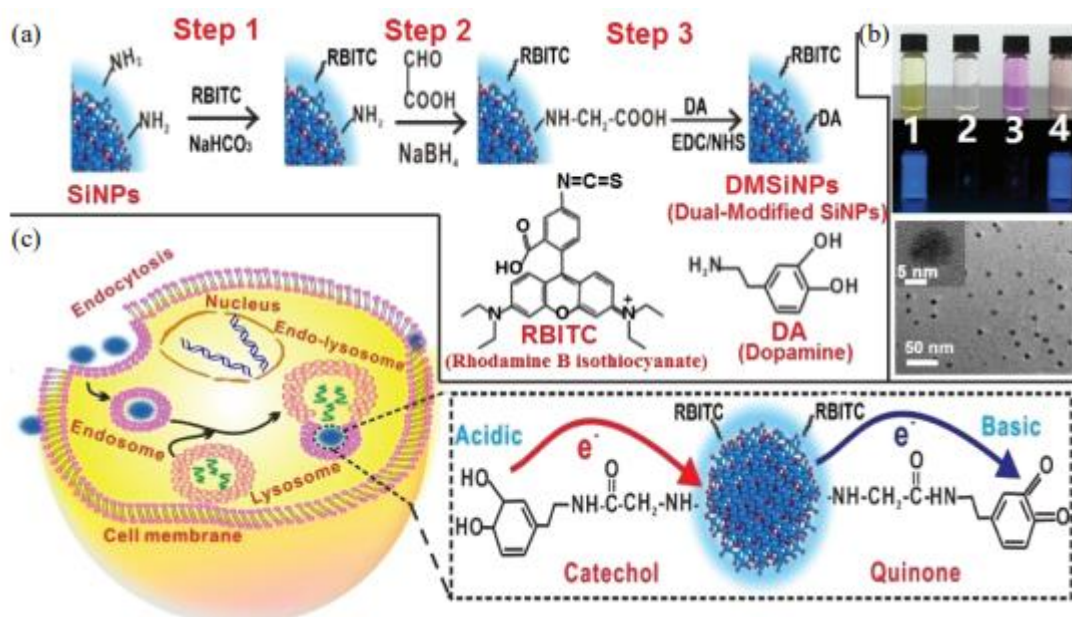


Figure 7. Construction of SiNPs-based intracellular pH sensor. (a) Schematic illustration of the synthesis of sensor. (b) Photos of SiNPs (1), dopamine (2), RBITC (3), and modified SiNPs (4) in ambient environment and under UV irradiation ($\lambda_{ex} = 360 \text{ nm}$) as well as TEM image of DMSiNPs. Inset shows the enlarged HRTEM image of a single DMSiNPs. (c) Schematic illustration of cellular internalizations of DMSiNPs. Inset in part C presents charge transfer mechanism of DMSiNPs at acidic or basic conditions.

Surface-Enhanced Raman Scattering on Silicon

Nanomaterials made of silicon have attracted a lot of interest in recent decades due to their unusual electrical, optical, and mechanical characteristics. Bioimaging and biosensing have both made extensive use of nanomaterials derived from silicon. Among these, sensors built on nano-hybrid SERS substrates made of silicon (such as silicon substrates enhanced with gold or silver nanoparticles) exhibit excellent repeatability and sensitivity. It is easy to observe that the SERS substrate made of pure gold/silver nanoparticles has a lower EF value and somewhat poor reproducibility when compared to the silicon-based nano-hybrid SERS substrates. The detection sensitivity is improved, however, since the SERS enhancement effect is realised by the effective coupling of plasmon resonance scattered by metal nanoparticles and plasmon resonance reflected from semiconductor silicon surface in silicon-based nanohybrid substrates. From 80 to 82 plus 90 To improve repeatability and prevent the random aggregation of free gold/silver nanoparticles, silicon-based nanohybrid materials have metal nanoparticles firmly attached to silicon substrates. In order to build novel high-

quality biosensors, a variety of nanohybrid substrates based on silicon have been created. Here we shall describe the design and preparation procedures of silicon nanohybrid-based SERS substrates, go into detail about the unique advantages of these substrates [39-42], and then leave it at that. The following section provides an overview of various SERS sensors that are based on silicon nanohybrids. It then goes on to demonstrate how these sensors can detect chemical and biological samples with unprecedented sensitivity, selectivity, and reproducibility. Lastly, we will go over the difficulties and potential advancements of SERS sensors built on silicon nanohybrids as a novel testing and analysis platform.

Characteristics of Surface-Enhanced Raman Scattering on Silicon

Two primary features of SERS substrates made of silicon nanohybrid materials stand out: first, the substrates significantly improve SERS signals, and second, the signals may be reproduced with relative ease. Not only does metal nanoparticles interact with one another via plasmon resonance, but they also effectively couple with neighbouring silicon substrates (semiconductors) [43, 44], which enhances SERS. The connection between SERS substrates made of silicon and the related SERS amplification effect at the nanoparticle level was studied by He and colleagues in 2014. When R6G is adsorbed onto gold nanoparticles modified on a silicon wafer substrate, the Raman signal (curve I) is stronger than when it is adsorbed onto quartz glass. Furthermore, the calculation shows that the EF value of the Raman signal on a silicon substrate that has been modified with gold nanoparticles is 2.5×10^4 , which is greater than the EF value of the Raman signal on a quartz glass substrate (3.0×10^2). The computed results further confirm experimental observations by simulating this system using finite-difference time-domain (FDTD). Near the interface of the gold nanoparticle and the silicon substrate, there is a maximum enhancement position of the normalised electromagnetic field (EM-field) ($|E|^2/|E_0|^2$, $|E|^2$ and $|E_0|^2$, representing the intensity of the scattered and incident electromagnetic fields, respectively). Metal nanoparticles can augment the electromagnetic field via plasmonic interaction, which also occurs through plasmonic resonance coupling with neighbouring silicon substrates. In the space between the two surfaces, the electromagnetic field is amplified to a much greater extent. The normalised electromagnetic field intensity can be increased by a factor of 21.3 when gold nanoparticles (satellites) and silver nanoparticles (core) are mixed. This is approximately 4.6 times stronger than the enhancement effect of pure silver nanoparticles distributed on a silicon wafer. Meanwhile, SERS substrates made of silicon-based nanohybrids effectively limit the nanoparticles' random mobility and agglomeration by the direct fixation of metal nanoparticles [45-49] onto the silicon wafer, resulting in excellent repeatability. To conclude, silicon-based nanohybrids have the potential to become an effective analytical platform in real-world applications due to their high sensitivity and excellent reproducibility.

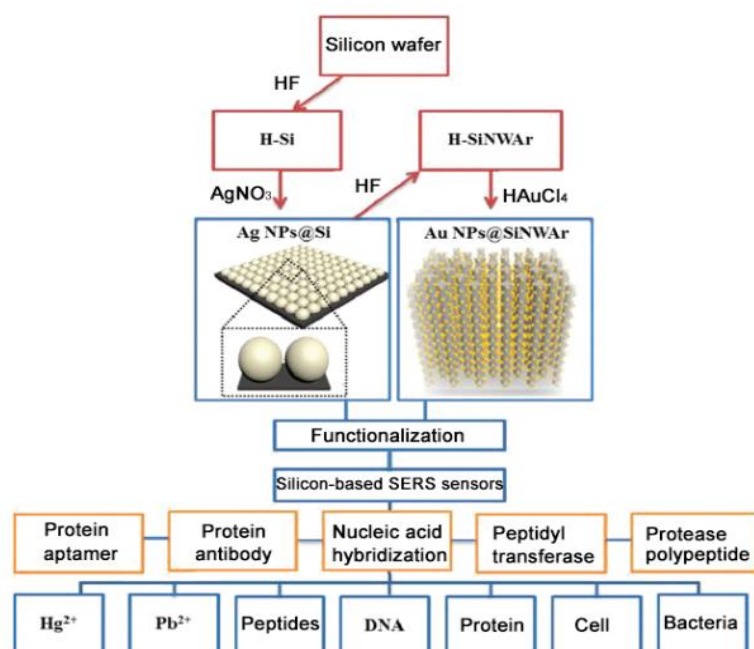


Figure 8. SERS substrates constructed using two-dimensional and three-dimensional silicon nano-hybrid materials (silver nanoparticles modified silicon wafer (AgNP@Si) and gold nanoparticles modified silicon nanowire array (AuNP@SiNWA)) and SERS sensors for different purposes constructed after functionalization.

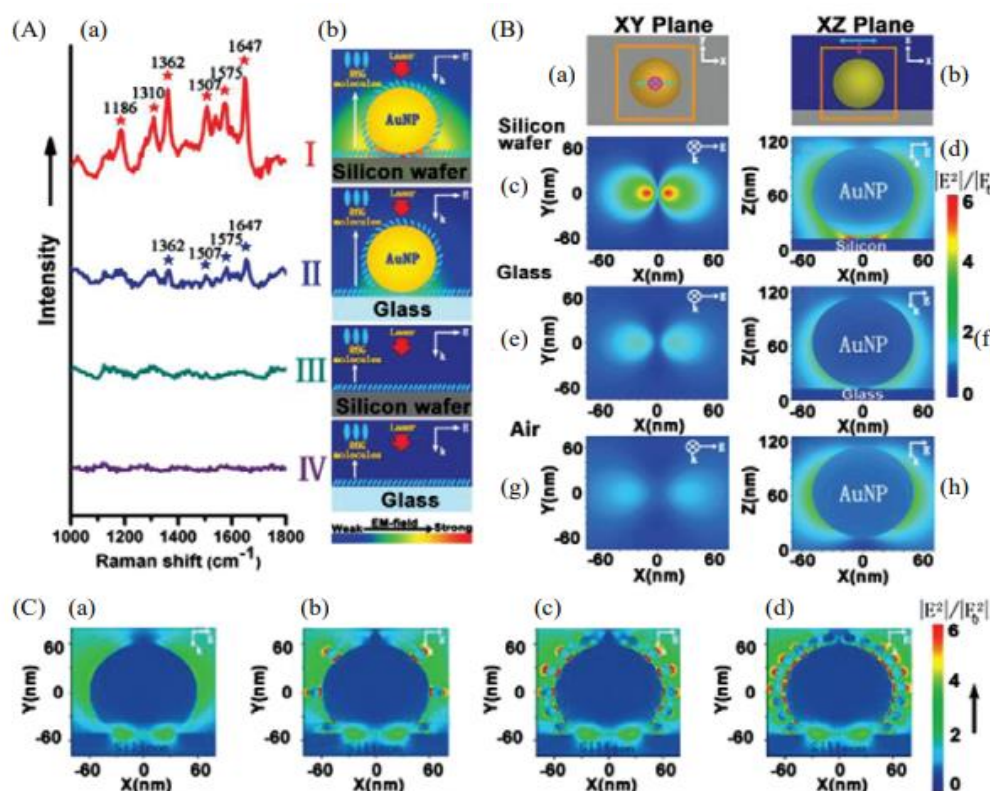


Figure 9. (a) SERS spectra of R6G molecules on different substrates: silicon (vertical curve I), quartz glass (vertical curve II), bare silicon (vertical curve III), and quartz glass (vertical curve IV). (b) Intensity of electromagnetic fields (EMFs) experienced by R6G molecules adsorbed on a single gold nanoparticle on various substrates: silicon (I), quartz glass (II), bare silicon (III), and bare quartz glass (IV). The direction of the incident laser's propagation is shown by arrow k , while its polarisation is represented by arrow E . (B) FDTD model of the distribution of EM field intensity for a single gold nanoparticle in various dielectric settings. The XY plane (a) is perpendicular to the substrate via the centre of the gold nanoparticle, and the XZ plane (b) is above the 1nm underlying substrate. The pink arrow pointing in the z-direction indicates that the incident laser light has a wavelength of 514 nm. The direction of laser polarisation (along the x-axis) is indicated by the cyan arrow. An XY plane simulation of the normalised electromagnetic field intensity distribution ($|E|^2/|E_0|^2$) of a single gold nanoparticle on a silicon substrate (c), a quartz glass substrate (e), and air (g)

Advanced SERS Substrates Based on Silicon Nanohybrids

In this section, we will go over the layout and production of two common silicon nanohybrid SERS substrates: silicon nanowires (SiNWs) that have been adorned with gold and silver nanoparticles (AuNPs/AgNPs) and silicon wafer (Si) that has been covered with gold and silver nanoparticles.

Conductive SERS Active Substrates Based on Silicon Nanowires

As a crucial one-dimensional silicon nanostructure, silicon nanowires are now manufactured using one of four established methods: Methods for electroless metal catalytic etching, vapor-liquid-solid (VLS), chemical vapour deposition (CVD), oxide-assisted growth (OAG),¹⁰¹ and 102–108 Several reports in the literature have discussed these four types of preparation. Using a more developed oxidation-reduction reaction process, metal nanoparticles can be added to silicon nanowires made using the previous method. To create silicon nanowires with metal nanoparticles attached, hydrofluoric acid can be used to erode the surface of the nanowires with free metal ions present in the

reaction (Half-cell reaction: $\text{Si} + 6\text{F}^- \rightarrow \text{SiF}_6^{2-} + 4\text{e}^-$). By utilising in-situ growth of gold nanoparticles on the surface of silicon nanowires⁸⁰ in 2013, He et al. succeeded in creating a SERS substrate of silicon nanoparticles modified with gold nanoparticles (AuNPs@SiNWs) with an EF value ranging from 106 to 108. The size and distribution of the nanoparticles were customisable. Furthermore, a wide range of hybrid materials based on silicon nanowires and created by nanogold modification of various nanostructures (including spherical nanoparticles, cylindrical nanorods, triangular prism nanorods, and nanoparticle dimers) are being developed at a rapid pace and exhibiting promising SERS performance [50, 51]. A Raman signal approximately 24 times stronger than the inherent Raman signal was detected when silicon nanowires were treated with a nano-gold dimer and subjected to a stronger magnetic field. Simultaneously, points perpendicular to and parallel to the silicon wires are used to measure the Raman signal for the structure of gold nanorod-modified silicon nanowires. The results show that the Raman signals are stronger for silicon nanowires that have been changed in parallel with gold nanorods. First of its kind, this study proves that antenna effect can boost surface plasmons and gives useful data for investigating the mechanism of Raman amplification. Increasing the EF value of SERS substrates is the subject of numerous recent publications that discuss surface modification of silicon nanowires using silver nanoparticles. The surface of silicon nanowires is coated with a significant number of silver nanoparticles, as shown in images of transmission electron microscopy and atomic force microscopy of silicon nanowires modified by silver nanoparticles (AgNPs@SiNWs). On top of that, using silicon nanowire as a semiconductor to efficiently couple silver nanoparticles to its surface creates SERS hot spots, which greatly enhances SERS signals.⁸⁰ Along with the previously mentioned method of coating individual silicon nanowires with silver nanoparticles, Lee and colleagues in 2010 also developed a method of modifying silicon nanoarrays with silver nanoparticles and arranging silicon nanowires in an ordered fashion.

CONCLUSION

In conclusion, this study surveyed the most recent noteworthy advancements in the creation of optical biochemical sensors based on silicon, with a focus on fluorescence sensors based on zero-dimensional silicon nanoparticles and SERS sensors based on two-dimensional silicon nanohybrids. From one angle, there are several study papers based on various quantum dot sensors, and although there are a number of analytical instances that can be recognised by fluorescence sensors based on silicon nanoparticles, this field is still in its early stages. When it comes to building databases, SERS substrates based on silicon nanohybrids have a lot of benefits, such as a noninvasive data capture technique, strong anti-interfering ability, abundant and unique intrinsic fingerprint information, and more. Thus, silicon nanohybrids chips demonstrate great promise as a tool for building large and trustworthy databases, which could aid AI in making decisions regarding quick and accurate clinical diagnoses. Silicon nanohybrids-based SERS sensors still face numerous significant problems and hurdles, notwithstanding the accomplishments described before. To start, there has to be more detail provided regarding how silicon supports SERS enhancement. Secondly, it is still difficult to synthesise the silicon-based nanohybrid substrate with the desired morphology (e.g., length, diameter, size distribution, etc.) in a controlled manner. Third, there is a high need for the creation of innovative wearable or portable SERS sensors based on silicon nanohybrids to meet the needs of point-of-care or on-site detection. The silicon-based nano-hybrid SERS sensor is anticipated to construct a more dependable and potent analysis and detection platform that will see extensive usage in the future, subject to the satisfactory resolution of these issues.

REFERENCES

1. Tan, J.; Xu, L.; Li, T.; Su, B.; Wu, J. WuImage-Contrast Technology Based on the Electrochemiluminescence of Porous Silicon and Its Application in Fingerprint Visualization. *Angew. Chem. Int. Ed.* 2014, 53, 9822–9826.
2. Lin, G.; Ding, H.; Yuan, D.; Wang, B.; Wang, C. A Pyrene-Based, Fluorescent Three-Dimensional Covalent Organic Framework. *J. Am. Chem. Soc.* 2016, 138, 3302–3305.
3. Wang, B.; Lv, X. L.; Feng, D.; Xie, L. H.; Zhang, J.; Li, M.; Xie, Y.; Li, J. R.; Zhou, H. C. Highly Stable Zr(IV)-Based Metal-Organic Frameworks for the Detection And Removal of Antibiotics and Organic Explosives in Water. *J. Am. Chem. So.* 2016, 138, 6204–6216.

4. Yan, X.; Wang, H.; Hauke, C. E.; Cook, T. R. A Suite of Tetraphenylethylene-Based Discrete Organoplatinum(II) Metallacycles: Controllable Structure and Stoichiometry, Aggregation-Induced Emission, and Nitroaromatics Sensing. *J. Am. Chem. Soc.* 2015, 137, 15276–15286.
5. Myers, T. W.; Bjorgaard, J. A.; Brown, K. Energetic Chromophores: Low-Energy Laser Initiation in Explosive Fe(II) Tetrazine Complexes. *J. Am. Chem. Soc.* 2016, 138, 4685–4692.
6. Mosca, L.; Karimi Behzad, S.; Anzenbacher, P.; Jr. Small-Molecule Turn-On Fluorescent Probes for RDX. *J. Am. Chem. Soc.* 2015, 137, 7967–7969.
7. Geng, Y.; Ali, M. A.; Clulow, A. J.; Fan, S.; Burn, P. L.; Gentle, I. R.; Meredith, P.; Shaw, P. E. Selectively Detection of Explosives Using Fluorescent Dendrimer. *Nat. Commun.* 2015, 6, 8240.
8. Ben-Jaber, S.; Peveler, W. J.; Quesada-Cabrera, R.; Cortés, E.; SoteloVazquez, C; Abdul-Karim, N.; Maier, S. A.; Parkin, I. P. Photo-Induced Enhanced Raman Spectroscopy for Universal Ultra-Trace Detection of Explosives, Pollutants and Biomolecules. *Nat. Commun.* 2016, 7, 12189.
9. Carron, K.; Cox, R. Qualitative Analysis and the Answer Box: A Perspective on Portable Raman Spectroscopy. *Anal. Chem.* 2010, 82, 3419–3425
10. Han, Z.; Liu, H.; Meng, J.; Yang, L.; Liu, J. Portable Kit for Identification and Detection of Drugs in Human Urine Using SurfaceEnhanced Raman Spectroscopy. *Anal. Chem.* 2015, 87, 9500–9506.
11. Karabeber, H.; Huang, R.; Iacono, P.; Samii, J. M.; Pitter, K.; Holland, E. C.; Kircher, M. F. Guiding Brain Tumor Resection Using SurfaceEnhanced Raman Scattering Nanoparticles and a Hand-Held Raman Scanner. *ACS Nano* 2014, 8, 9755–9766.
12. Fujisawa, T.; Kuramochi, H.; Hosoi, H.; Takeuchi, S.; Tahara, T. Role of Coherent Low Frequency Motion in Excited State Proton Transfer of Green Fluorescent Protein Studied by Time-Resolved Impulsive Stimulated Raman Spectroscopy. *J. Am. Chem. Soc.* 2016, 138, 3942– 3945.
13. Chen, N.; Ding, P.; Shi, Y.; Jin, T.; Su, Y.; Wang, H.; He, Y. Portable and Reliable Surface-Enhanced Raman Scattering Silicon Chip for Signal-On Detection of Trace Trinitrotoluene Explosive in Real Systems. *Anal. Chem.* 2017, 89, 5072–5078.
14. Gopalakrishnan, D.; Dichtel, W. R. Direct Detection of RDX Vapor Using a Conjugated Polymer Network. *J. Am. Chem. Soc.* 2013, 135, 8357–8362.
15. Rose, A.; Zhu, Z.; Madigan, C. F.; Swager, T. M.; Bulović, V. Sensitivity Gains in Chemosensing by Lasing Action in Organic Polymers. *Nature* 2005, 434, 876.
16. Zhou, Q.; Swager, T. M. Method for Enhancing the Sensitivity of Fluorescent Chemosensors: Energy Migration in Conjugated Polymers. *J. Am. Chem. Soc.* 1995, 117, 7017–7018.
17. Liu, H.; Lin, D.; Sun, Y.; Yang, L.; Liu, J. Cetylpyridinium Chloride Activated Trinitrotoluene Explosive Lights Up Robust and Ultrahigh Surface-Enhanced Resonance Raman scattering in a silver sol *Chem. A Eur. J.* 2013, 19, 8789–8796.
18. Kneipp, K.; Wang, J.; Yang, L.; Liu, B.; Jiang, H.; Liu, R.; Yang, J.; Han, G.; Mei, Q.; Zhang, Z. Inkjet-Printed Silver Nanoparticle Paper Detects Airborne Species from Crystalline Explosives and Their Ultra-Trace Residues in Open Environment. *Anal. Chem.* 2014, 86, 3338–3345.
19. Gao, D.; Zhang, Z.; Wu, M.; Xie, C.; Guan, G.; Wang, D. A Surface Functional Monomer-Directing Strategy for Highly Dense Imprinting of TNT at Surface of Silica Nanoparticles. *J. Am. Chem. Soc.* 2007, 129, 7859–7866. b4257 V2_Ch-05.indd 304 27-05-2021
20. Tu, R.; Liu, B.; Wang, Z.; Gao, D.; Wang, F.; Fang, Q.; Zhang, Z. Amine-Capped ZnS-Mn²⁺ Nanocrystals for Fluorescence Detection of Trace TNT Explosive. *Anal. Chem.* 2008, 80, 3458–3465.

21. Zhou, H.; Zhang, Z.; Jiang, C.; Guan, G.; Zhang, K.; Mei, Q.; Liu, R.; Wang S. Trinitrotoluene Explosive Lights Up Ultrahigh Raman Scattering of Nonresonant Molecule on a Top-Closed Silver Nanotube Array. *Anal. Chem.* 2011, 83, 6913–6917.
22. Yang, L.; Ma, L.; Chen, G.; Liu, J.; Tian, Q. Z. Ultrasensitive SERS Detection of TNT by Imprinting Molecular Recognition Using a New Type of Stable Substrate. *Chem.–Eur. J.* 2010, 16, 12683–12693.
23. Witlicki, E. H.; Andersen, S. S.; Hansen, S. W.; Jeppesen, J. O.; Wong, E. W.; Jensen, L.; Flood, A. H. Turning on Resonant SERRS Using the Chromophore–Plasmon Coupling Created by Host–Guest Complexation at a Plasmonic Nanoarray. *J. Am. Chem. Soc.* 2010, 132, 6099–6107.
24. Zhang, M.; Zhao, L. B.; Luo, W. L.; Pang, R.; Zong, C.; Zhou, J. Z.; Ren, B.; Tian, Z. Q.; Wu, D. Y. Experimental and Theoretical Study on Isotopic Surface-Enhanced Raman Spectroscopy for the Surface Catalytic Coupling Reaction on Silver Electrodes. *J. Phys. Chem. C* 2016, 120, 11956–11965.
25. Huang, Y. F.; Zhu, H. P.; Liu, G. K.; Wu, D. Y.; Ren, B.; Tian, Z. Q. When the Signal is Not from the Original Molecule to Be Detected: Chemical Transformation of para-Aminothiophenol on Ag during the SERS Measurement. *J. Am. Chem. Soc.* 2010, 132, 9244–9246.
26. Zhang, M. L.; Yi, C. Q.; Fan, X.; Peng, K. Q.; Wong, N. B.; Yang, M. S.; Lee, S. T. A Surface-Enhanced Raman Spectroscopy Substrate for Highly Sensitive Label-Free Immunoassay. *Appl. Phys. Lett.* 2008, 92, 043116.
27. Yi, C.; Li, C. W.; Zhang, H.; Fu, M.; Qi, S.; Wong, N.-B.; Lee, S. T.; Yang, M. Patterned Growth of Vertically Aligned Silicon Nanowire Arrays for Label-Free DNA Detection Using Surface-Enhanced Raman Spectroscopy. *Anal. Bioanal. Chem.* 2010, 397, 3143.
28. Wang, H.; Jiang, X.; Wang, X.; Wei, X.; Zhu, Y.; Sun, B.; Su, Y.; He, S.; He, Y. Hairpin DNA-Assisted Silicon/Silver-Based Surface-Enhanced Raman Scattering Sensing Platform for Ultrahighly Sensitive and Specific Discrimination of Deafness Mutations in a Real System. *Anal. Chem.* 2014, 86, 7368–7376.
29. Biochemical Sensors (in 2 parts) “9x6” 306 Biochemical Sensors NB&A 177. Efrima, S.; Zeir, i L. J. Understanding SERS of Bacteria. *Raman Spectrosc.* 2009, 40, 277.
30. Xu, L. J.; Lei, Z. C.; Li, J.; Zong, C.; Yang, C. J.; Ren, B. Label-Free Surface-Enhanced Raman Spectroscopy Detection of DNA with Single-Base Sensitivity. *J. Am. Chem. Soc.* 2015, 137, 5149–5154.
31. Chen, H. Y.; Lin, M. H.; Wang, C. Y.; Chang, Y. M.; Gwo, S. LargeScale Hot Spot Engineering for Quantitative SERS at the Single-Molecule Scale. *J. Am. Chem. Soc.* 2015, 137, 13698–13705.
32. Zhang, Y.; Zou, Y.; Liu, F.; Xu, Y.; Wang, X.; Li, Y.; Liang, H.; Chen, L.; Chen, Z.; Tan, W. Stable Graphene-Isolated-Au-Nanocrystal for Accurate and Rapid Surface Enhancement Raman Scattering Analysis. *Anal. Chem.* 2016, 88, 10611–10616.
33. Wang, Y.; Yan, B.; Chen, L. SERS Tags: Novel Optical Nanoprobes for Bioanalysis. *Chem. Rev.* 2013, 113, 1391–1428.
34. Miller, S.; Tavshanjian, B.; Oleksy, A.; Perisic, O.; Houseman, B. T.; Shokat, K. M.; Williams, R. L. Shaping Development of Autophagy Inhibitors with the Structure of the Lipid Kinase Vps34. *Science* 2010, 327, 1638–1642.
35. Huang, S. C.; Artyukhin, A. B.; Misra, N.; Martinez, J. A.; Stroeve, P. A.; Grigoropoulos, C. P.; Ju, J. W.; Noy, A. Carbon Nanotube Devices Controlled by an Ion Pump Gate. *Nano Lett.* 2010, 10, 1812–1816.
36. Vilchez, D.; Saez, I.; Dillin, A. The Role of Protein Clearance Mechanisms in Organismal Ageing and Age-Related Diseases. *Nat. Commun.* 2014, 5, 5659. 207. Shi, H.; Chen, N.; Su, Y.; Wang, H.; He, Y. *Anal. Chem.* 2017, 89, 10279–10285.
37. Smith, Z. D.; Meissner, A. DNA methylation: roles in mammalian development. *Nat. Rev. Genet.* 2013, 14, 204–220. b4257 V2_Ch-05.indd 308 27-05-2021

38. PM “9x6” b4257 Biochemical Sensors (in 2 parts) Silicon-Based Optical Biochemical Sensors 309 209. Lui, C. H.; Liu, L.; Mak, K. F.; Flynn, G. W.; Heinz, T. F. Ultraflat Graphene. *Nature* 2009, 462, 339–341.
39. Kim, K.; Choi, J. Y.; Kim, T.; Cho, S. H.; Chung, H. J. AA Role for Graphene in Silicon-based Semiconductor Devices. *Nature* 2011, 479, 338–344.
40. Song, Z. L.; Chen, Z.; Bian, X.; Zhou, L. Y.; Ding, D.; Liang, H.; Zou, Y. X.; Wang, S. S.; L. Yang, Chen, C.; Zhang, X. B.; Tan, W.; Focus on Performance of Perovskite Light-emitting Diodes. *J. Am. Chem. Soc.* 2014, 136, 13558–13561.
41. LeCun; Y.; Bengio; Y.; Hinton; G. Deep Learning. *Nature* 2015, 521, 436–444.
42. Hinton, G. E.; Osindero, S.; Teh, Y. W. A Fast Learning Algorithm for Deep Belief Nets. *Neural Comput.* 2006, 18, 1527–1554.
43. Silver, D.; Huang, A.; Maddison, C. J.; Guez, A.; Sifre, L.; van den Driessche, G.; Schrittwieser, J.; Antonoglou, I.; Panneershelvam, V.; Lanctot, M.; Dieleman, S.; Grewe, D.; Nham, J.; Kalchbrenner, N.; Sutskever, I.; Lillicrap, T.; Leach, M.; Kavukcuoglu, K.; Graepel, T.; Hassabis, D. Mastering the Game of Go with Deep Neural Networks and Tree Search. *Nature* 2016, 529, 484–489.
44. Mnih, V.; Kavukcuoglu, K.; Silver, D.; Rusu, A. A.; Veness, J. Human Level Control through Deep Reinforcement Learning. *Nature* 2015, 518, 529–533.
45. Lake, B. M.; Salakhutdinov, R.; Tenenbaum, J. B. Human-Level Concept Learning through Probabilistic Program Induction. *Science* 2015, 350, 1332–1338.
46. Kermany, D. S.; Goldbaum, M.; Cai, W. Identifying Medical Diagnoses and Treatable Diseases by Image-Based Deep Learning. *Cell* 2018, 172, 1122–1131.
47. Yang, H.; Qi, D.; Liu, Z.; Chandran, B. K.; Wang, T.; Yu, J.; Chen, X. Soft Thermal Sensor with Mechanical Adaptability. *Adv. Mater.* 2016, 28, 9175–9181.
48. Najafabadi, M. M.; Villanustre, F.; Khoshgoftaar, T. M.; Seliya, N.; Wald, R.; Muharemagic, E. Deep Learning Applications and Challenges in Big Data Analytics. *J. Big Data* 2015, 2, 1–21.
49. Yin, S.; Kaynak, O. Proc. Big Data for Modern Industry: Challenges and Trends. *IEEE* 2015, 103, 143–146.
50. Russakovsky, O.; Deng, J.; Su, H.; Krause, J. Imagenet Large Scale Visual Recognition Challenge. *Int. J. Comput. Vis.* 2015, 115, 211–252.
51. . Shen, Q.; Jiang, J. H.; Jiao, C. X.; Lin, W. Hybridized Particle Swarm Algorithm for Adaptive Structure Training of Multilayer Feed-Forward Neural Network: QSAR Studies of Bioactivity of Organic Compounds. *J. Comput. Chem.* 2004, 25, 1726–1735.
52. Wang, B.; Cancilla, J. C.; Torrecilla, J. S.; Haick, H. Effect of Functional Groups on the Sensing Properties of Silicon Nanowires toward Volatile Compounds. *Nano Lett.* 2014, 14, 933–938.
53. Shi, H.; Wang, H.; Meng, X.; Chen, R.; Zhang, Y.; Su, Y.; He, Y. Setting Up a Surface-Enhanced Raman Scattering Database for Artificial-Intelligence-Based Label-Free Discrimination of Tumor Suppressor Genes. *Anal. Chem.* 2018, 90, 14216–14221.