

## MINIREVIEW

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# The emerging role of semiconductor nano-photocatalysts in strengthening surface enhanced Raman scattering applicability for sustainable multifunctional applications

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Surface-enhanced Raman scattering (SERS) has emerged as a powerful analytical technique for the ultrasensitive detection of organic, inorganic, and biological molecules, with promising applications in environmental monitoring, biomedical diagnostics, and chemical analysis. Traditionally, noble metal nanostructures have served as key SERS substrates due to their localized surface plasmon resonance driven electromagnetic enhancement. However, evolving application requirements including operational durability, sustainability considerations, and economic factors have driven the exploration of complementary materials to expand and diversify SERS platform capabilities. In response, semiconductor-based nano-photocatalysts have attracted growing interest as complementary materials in SERS substrate design. These materials offer distinct advantages, including photocatalytic activity, efficient surface adsorption and self-cleaning as well as charge transfer capabilities—enhancing the SERS sensitivity, reproducibility, and structural robustness. Furthermore, they enable real-time monitoring of photocatalytic molecular transformations and reaction intermediates, contributing valuable insights into surface chemistry and charge-transfer mechanisms. Hybrid SERS substrates, combining semiconductor photocatalysts with noble metal nanostructures, provide synergistic SERS enhancement effects through

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gious CSIR Junior Research Fellowship award. His research has already made significant contributions to the scientific community, with publications in renowned journals such as *ACS Langmuir*, *Chemosphere*, *ChemComm*, *Advanced Powder Materials* etc. His work promises to push the boundaries of material science and contribute to address critical challenges in sustainable energy and environmental solutions.



the integration of electromagnetic and chemical (or charge transfer) mechanisms while also improving the optoelectronic properties and expanding the functionality in other directions. The incorporation of emerging photocatalytic materials such as UV- and visible-light-active semiconducting materials, semiconducting polymeric and two-dimensional semiconducting materials with special features/characteristics like thermoelectric, magnetic and self-cleaning properties further strengthens SERS applicability by offering greater flexibility, multifunctionality, and sustainability. This minireview highlights the emerging role of such semiconductor nano-photocatalysts in advancing SERS technology toward sustainable multifunctional applications. It discusses recent advances, current challenges, and future strategies aimed at enhancing SERS efficiency and broadening its utility in environmental, biomedical, and catalytic domains.

## 1. Introduction

The year 2024 was celebrated as the 50th anniversary of the discovery of surface-enhanced Raman spectroscopy (SERS).<sup>1–3</sup> SERS is a surface sensitive scientific tool measuring the enhanced Raman signals from an analyte molecule adsorbed on the surface of a nanostructured material under the influence of laser irradiation from a Raman spectrophotometer (Fig. 1). SERS has been found to be a popular ultra-detection method for a variety of molecular species in environmental monitoring and wastewater treatment as well as in biomedical research.<sup>4,5</sup> In recent years, there has been growing interest of the scientific community in developing and designing SERS materials/substrates with higher sensitivity, durability/stability and recyclability for long-term applications.<sup>6–10</sup> A great deal of research has been conducted with excellent results as reported in the literature.<sup>4–6,9–15</sup> Generally, noble metals nanostructures (NMNs) are known to be the best SERS substrates because of their localized surface plasmon resonance (LSPR) properties.<sup>13,16</sup> SERS is primarily reported as contribution from

electromagnetic (EM) enhancement attributed to the LSPR properties of NMNs, which amplifies the Raman signals. This model does not rely on specific chemical bonding between the adsorbate and the NMNs. It accounts for phenomena such as enhanced signals occurring at a distance from the metal surface and the angular dependence of the enhancement relative to the direction of the incoming radiation. This mechanism can explain realistic EM enhancement factors of up to  $10^4$ . However, noble metals also present certain practical limitations, such as poor thermal and chemical stability in harsh environments, susceptibility to surface fouling, limited recyclability, and high cost, which have been documented in previous studies.<sup>17</sup> These challenges restrict their long-term use in sustainable or regenerative SERS platforms. Another mechanism that contributes to the SERS signals is the chemical (CM) enhancement attributed to the charge transfer (CT) mechanism, particularly shown by semiconductor nanostructures.<sup>18,19</sup> It involves various CT interactions between the semiconductor surface and adsorbed molecules, particularly through vibronic coupling as proposed by Herzberg-Teller and further elaborated by Lombardi.<sup>20–24</sup> In



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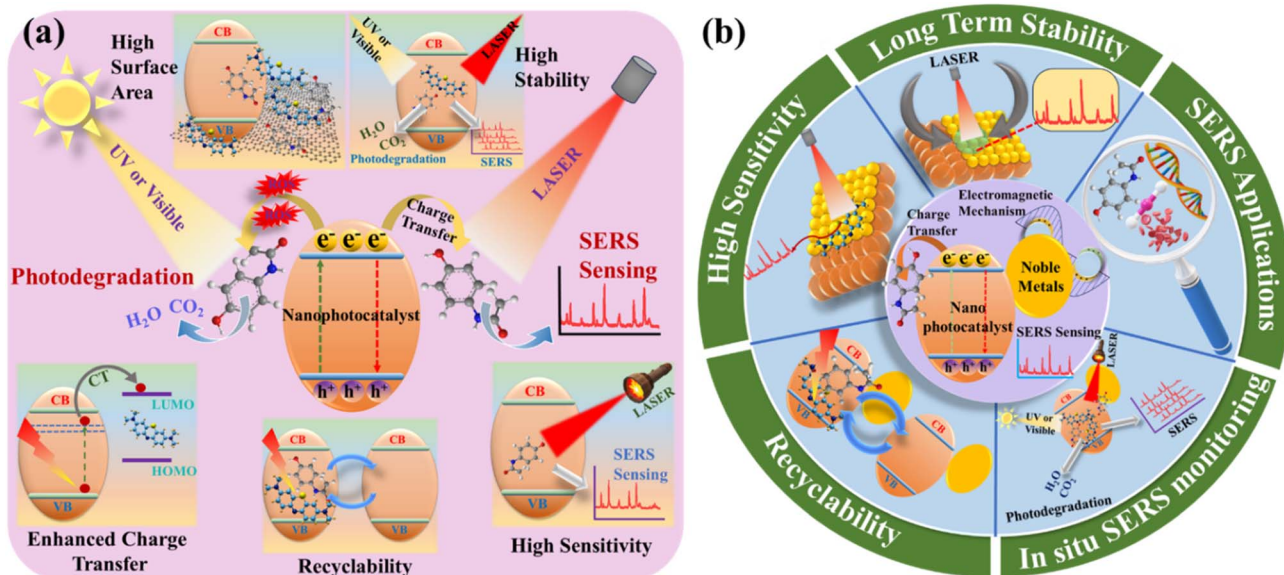


Fig. 1 Schematic: (a) role of novel semiconductor-only nano-photocatalysts in strengthening SERS detection activity and (b) improved SERS and multifunctional activities of nano-photocatalysts when combined with noble metals.

1983, Yamada *et al.*<sup>25</sup> made a significant contribution to SERS research reporting on the first SERS activity by a semiconductor material with remarkable enhancement of pyridine's Raman signal when adsorbed on a NiO substrate.<sup>25</sup> This work expanded the scope of SERS to include semiconductor materials, which was traditionally associated only with NMNs such as Au and Ag nanostructures. Later, SERS research on semiconductor materials flourished with a focus on a variety of metal oxides and other semiconductor photocatalysts, including ZnO,<sup>6</sup> TiO<sub>2</sub>,<sup>26,27</sup> Fe<sub>2</sub>O<sub>3</sub>,<sup>28</sup> CuO,<sup>29</sup> Ta<sub>2</sub>O<sub>5</sub>,<sup>12</sup> CdS,<sup>30</sup> ZnSe,<sup>31</sup> *etc.*, in addition to emerging two-dimensional (2D) nanomaterials such as graphene oxide (GO),<sup>32,33</sup> MoS<sub>2</sub> (ref. 34 and 35), *etc.*

The development of semiconductor-based SERS substrates also encouraged the modification of semiconductor materials through surface activation/defects and doping with metals/non-metals as well as integration with NMNs, which further improve the Raman signal enhancement.<sup>6,27,36</sup> However, SERS sensitivity, stability and particularly recyclability for long-term practical applications still remain challenging, especially in the case of NMN-based SERS substrates, which have been investigated very seriously in the last few decades.<sup>10,15</sup> In this context, various strategies have been implemented for achieving higher sensitivity and stability as well as recyclability by engineering the shape, size, and dimensions (0–3D) of NMNs and semiconductors or coupling these nanomaterials together or further with other functional nanomaterials. In particular, nano-photocatalyst semiconductors are found to be more interesting in view of their sole SERS functionality as well as their emerging role in strengthening SERS ultra-detection applicability of NMNs towards multifunctionality. Semiconductor nano-photocatalysts, with their inherent ability to interact with light, charge carriers, and molecular adsorbates as well as their self-cleaning ability (*i.e.* through photodegradation of adsorbed molecules on its surface), offer an innovative approach to

design noble metal free nano-photocatalyst-based SERS substrates with improved SERS sensitivity while addressing the long-standing issues of recyclability and stability in the case of NMNs. Semiconductor nano-photocatalysts offer unique advantages for SERS applications due to their high surface area, which enhances both analyte adsorption and charge separation, as illustrated in Fig. 1(a). When exposed to light excitation, these materials generate electron-hole pairs that enable a dual functionality: simultaneous photodegradation of contaminants and SERS sensing through charge-transfer interactions.<sup>37–39</sup> This dual mechanism is further enhanced by the combination of chemical and electromagnetic effects, resulting in sensors with high sensitivity, excellent stability, and recyclability.<sup>20,40–42</sup> The integration of nano-photocatalysts and metal components in hybrid nanostructures represents a significant advancement in SERS technology, as shown in Fig. 1(b). The nano-photocatalyst-metal hybrids synergistically combine photocatalytic activity with plasmonic effects, creating platforms capable of both efficient analyte detection and environmental remediation.<sup>43,44</sup> These hybrid systems offer several key advantages that strengthen the SERS performance. First, they exhibit enhanced photocatalytic activity through the Schottky effect at metal-semiconductor interfaces and localized surface plasmon resonance properties. Second, their synergistic SERS and photocatalysis capabilities enable real-time monitoring of chemical reactions and *in situ* molecular interaction studies. Additionally, their light-induced self-cleaning ability provides recyclable substrates through photodegradation of adsorbed molecules, while semiconductor coatings improve noble metal nanostructure stability, as shown in Fig. 1(b). In addition to these characteristics, diverse semiconductor nano-photocatalysts (*i.e.* polymeric, 2D, magnetic, *etc.*) with special features like magnetic, thermoelectric, and mechanical properties provide more flexible and sustainable SERS substrates with





multifunctional applications are reported in this minireview, which have rarely been reviewed previously.

## 2. SERS mechanisms and monitoring strategies

SERS achieves its extraordinary sensitivity through a combination of electromagnetic and chemical enhancement mechanisms. Electromagnetic enhancement is the dominant mechanism and is attributed to the excitation of LSPR in noble metal nanostructures, such as gold or silver.<sup>3</sup> When these nanostructures are illuminated, collective oscillations of conduction electrons generate intense localized electromagnetic fields, particularly at “hot spots”—nanoscale junctions or gaps between particles. When incident light ( $E_i$ ) excites the LSPR of NMNs, it induces strong local fields ( $E_{i,s}$ ), enhancing the total field to  $(E_i + E_{i,s})$ . This intensified field excites the nearby adsorbed molecules, boosting the Raman signal to  $(E_i + E_{i,s})^2$ . Similarly, the emitted Raman field ( $E_R$ ) is enhanced to  $(E_R + E_{R,s})^2$ . Thus, the overall Raman intensity increases by a factor of  $E^4$ , as illustrated in Fig. 2(a).<sup>3,45,46</sup> When the energy difference between the incident and scattered light is small, EM enhancement is often described using a near-field model that assumes a uniform field across the molecule.<sup>3</sup> However, for nanoparticles with atomic-scale growth, field gradient effects become significant, contributing additional enhancement from the inhomogeneous field. EM enhancement on metallic substrates can range from  $10^4$  to  $10^{10}$ , and because it arises from plasmon resonance, it is generally considered independent of the molecule's electronic structure.<sup>47</sup>

Unlike the EM, the CM is directly related to the electronic structure of the molecule on the surface. The CM SERS enhancement is achieved when multiple resonance conditions overlap: (i) the laser wavelength matches the molecular electronic transition ( $\lambda_{\text{laser}} = \lambda_{\text{mol}}$ ), (ii) Mie-type resonances occur due to nanoparticle morphology ( $\lambda_{\text{laser}} = \lambda_{\text{Mie}}$ ), and (iii) the laser also aligns with the CT resonance energy ( $\lambda_{\text{laser}} = \lambda_{\text{CT}}$ ) (Fig. 2(b and c)). This phenomenon, known as coupled resonance, is supported by Herzberg–Teller vibronic coupling, where vibrational modes gain intensity through electronic transitions.<sup>49</sup> Even when the laser is slightly off-resonance, intensity borrowing can occur from nearby excitonic or molecular resonances, still resulting in significant enhancement.<sup>18</sup> The choice of laser is a critical factor in SERS experiment design. The laser wavelength should ideally match the plasmon resonance of the SERS substrate, typically composed of gold or silver nanoparticles, to maximize electromagnetic enhancement. It is also important to select a wavelength that avoids fluorescence from the sample, which can obscure the Raman signal; near-infrared lasers, such as those operating at 785 nm, are often preferred for biological samples for this reason. For studies focused on charge transfer or resonance Raman effects, the laser should be chosen to match the electronic transition of the molecule or the charge transfer complex.<sup>18</sup>

Mie resonance, seen in dielectric particles and noble metal nanoparticles, boosts the local electromagnetic field when the particle size matches the light's wavelength, enhancing the

Raman signal. For noble metal-free substrates, the enhancement scales with the square of the scattering efficiency.<sup>50</sup> In molecular resonance, no substrate is required. When the excitation laser wavelength matches the energy gap between the molecule's HOMO and LUMO, a resonant Raman spectrum is produced, increasing the Raman intensity by 3–4 times.<sup>49</sup> In the CT mechanism, the analyte chemically adsorbs on the substrate, changing its polarizability and modifying its Raman spectra. SERS enhancement in semiconductors mainly comes from direct CT between the analyte and substrate, which requires matching energy levels. CT can occur *via* electrons moving from the analyte's HOMO to the semiconductor's conduction band, from the semiconductor's valence band to the analyte's LUMO, or through sub-band gap states. Other less common paths involve electron transfer between CT complexes and the semiconductor's conduction band<sup>51</sup> (Fig. 2(d)).

The ability to monitor chemical reactions on nanoparticle surfaces or within confined environments is of growing importance, both for advancing fundamental physicochemical knowledge and for enabling practical technological applications. Monitoring reactions with SERS relies on detecting changes in the vibrational spectra of molecules adsorbed on or near the substrate surface.<sup>50</sup> As a reaction unfolds, SERS can reveal shifts in Raman peak positions, which indicate changes in bonding or electron density, as well as intensity variations that may result from resonance effects or altered charge transfer efficiency. The appearance or disappearance of specific peaks can also be correlated with the formation or consumption of transient intermediates or products.<sup>52</sup> CT processes at interfaces can also be effectively probed using SERS. These processes are often evidenced by spectral shifts, reflecting changes in the electronic structure of the molecule due to electron movement between the molecule and the substrate.<sup>53</sup>

Several analytical tools are available for studying CT with SERS. Electrochemical SERS (EC-SERS), for instance, involves applying an external potential to drive and monitor redox or CT reactions at electrode surfaces, enabling direct observation of electron transfer processes.<sup>54</sup> Computational modeling, particularly density functional theory (DFT), is also commonly used to predict possible charge transfer pathways and to interpret observed spectral changes based on molecular orbital energies and substrate band structures.<sup>55</sup> A range of experimental tools and tests further enhance the ability of SERS to monitor dynamic processes. Dynamic or time-resolved SERS enables real-time tracking of reaction kinetics and the identification of transient species, even down to the single-molecule level.<sup>56</sup> Multimodal SERS platforms, which combine SERS with complementary techniques such as electrochemistry or microscopy, provide a more comprehensive analysis of reaction mechanisms and charge transfer dynamics. Additionally, flow systems allow for the continuous monitoring of reactions under controlled conditions, improving reproducibility and enabling detailed kinetic studies.<sup>57</sup>

In summary, SERS provides a versatile and sensitive platform for monitoring chemical reactions and charge transfer at surfaces. By thoughtfully selecting the substrate, laser wavelength, and experimental approach, researchers can obtain real-



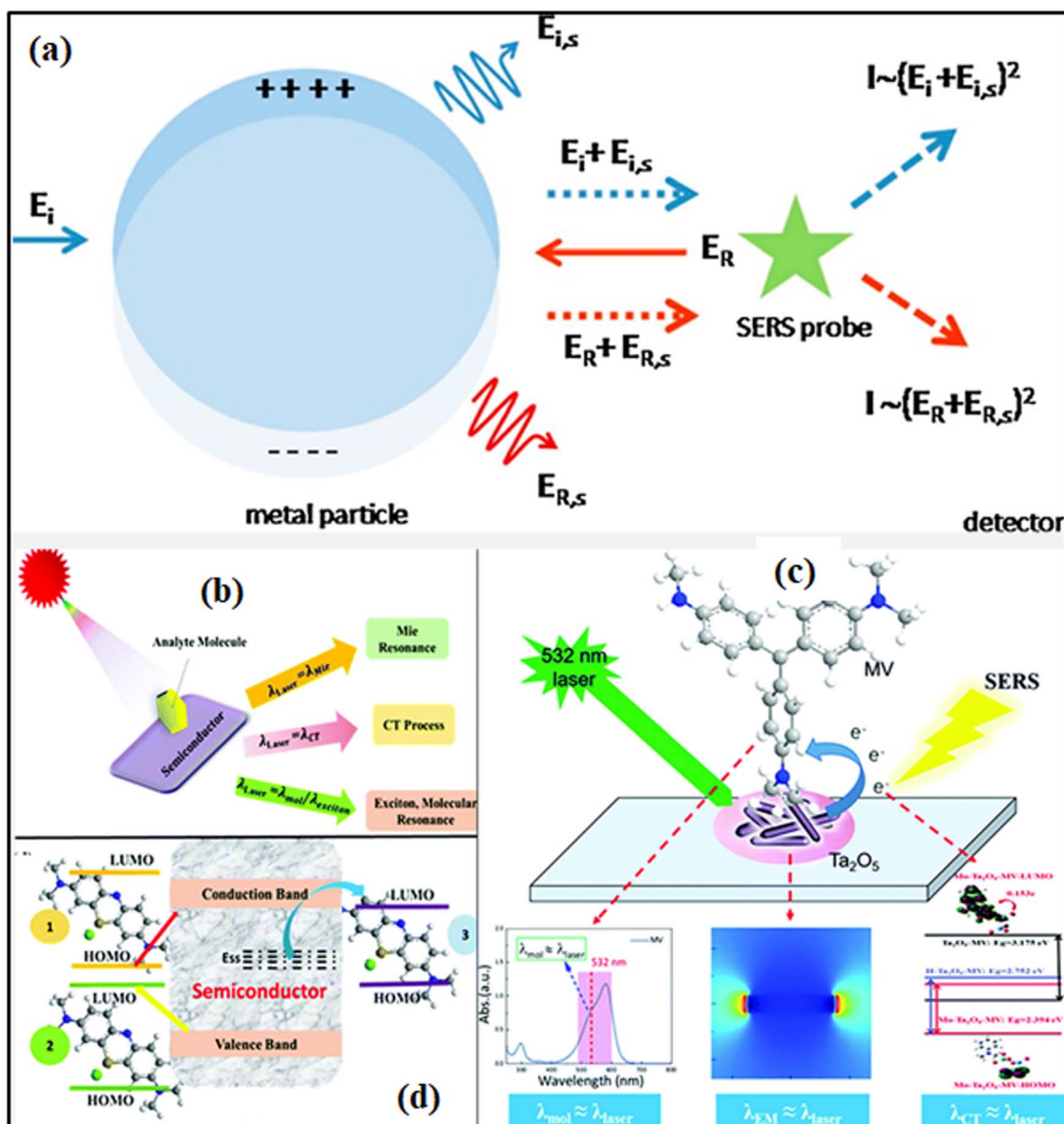


Fig. 2 (a) Schematic diagram depicting the electromagnetic enhancement process in SERS. Reprinted from open source access ref. 46. (b) Schematic illustrating tunable SERS enhancement in semiconductor systems (reprinted with permission from ref. 18. Copyright 2022, Royal Society of Chemistry). (c) Mechanism of the "coupled resonance" strategy on  $\text{Ta}_2\text{O}_5$ -based SERS substrates (reprinted from open source access ref. 48). (d) Possible CT pathways: (1) HOMO to CB, (2) VB to molecular LUMO, and (3) surface state to molecular LUMO (reprinted with permission from ref. 18. Copyright 2022, Royal Society of Chemistry).

time, molecular-level insights into dynamic processes that are often inaccessible by other analytical methods. This makes SERS an indispensable tool for advancing our understanding of interfacial chemistry and reaction mechanisms.

### 3. The role of nano-photocatalysts in strengthening SERS applicability for sustainable multifunctional applications

In recent years, semiconductor nano-photocatalysts have garnered attention as promising materials in diverse fields

including environmental remediation, energy conversion, chemical sensing, *etc.*<sup>58,59</sup> As discussed above, semiconductor materials offer notable self-cleaning ability, allowing for multiple uses which contribute to the sustainable long-term applications. The ability to engineer semiconductor band structures through doping, heterojunction formation, and surface modifications enables optimization of SERS performance of these materials tailored to specific needs. These innovations are essential for ensuring the long-term durability, structural stability, and sustainable recyclability of SERS substrates across diverse sensing and photocatalytic applications which have been discussed here.



### 3.1 Through surface/doping engineering of sole semiconductor photocatalysts for enhanced CT SERS activity

Doping engineering in semiconductor nano-photocatalysts optimizes their energy band gap and enhances the CT between the semiconductor substrates and target molecules. Recent advancements highlight the role of surface/doping engineering in improving the optical, electrical, structural, and surface properties for applications such as photocatalysis and SERS ultra-detection. By introducing foreign elements, doping transforms non-SERS active semiconductors into efficient SERS substrates by generating defects that increase the charge carrier density, modify lattice constants and bond energies, and tailor energy band gaps along with surface areas and defect contents.<sup>60</sup> These modifications/changes collectively enhance the CT efficiency, enabling superior SERS performance, in particular in semiconductor molecular systems.<sup>20</sup> For instance, recently, our group reported the hydrothermal synthesis of TiO<sub>2</sub> nanorods (NRs) and Ta-doped TiO<sub>2</sub> NRs (Fig. 3(a and b)) with enhanced optical and CT properties. Optimized TiO<sub>2</sub> NRs (band gap: 2.95 eV) and Ta-doped TiO<sub>2</sub> NRs (band gap: 2.58 eV) exhibited improved SERS activity for methylene blue (MB) detection (Fig. 3(c)), attributed to the synergistic effects of soaking treatment and Ta doping, which induced the surface/lattice defects and additional energy levels in TiO<sub>2</sub>.<sup>61</sup> The improved performance resulted from enhanced CT processes that were facilitated by surface defects and Ta-induced energy levels that acted as mediator states. Ta doping introduced defect states below the conduction band, which enabled efficient electron transfer and stabilized molecule interactions. This synergistic defect engineering and doping strategy significantly enhanced the optical and electronic properties of TiO<sub>2</sub>, establishing it as a cost-effective platform for sensitive molecular detection in environmental and biomedical applications.

Li *et al.*<sup>62</sup> studied that Sr doping in TiO<sub>2</sub> introduced surface oxygen vacancies and energy level defects, which significantly enhanced SERS activity with a detection limit of  $1 \times 10^{-9}$  M and enhancement factor (EF) of  $9.3 \times 10^6$  for 4-mercaptobenzoic acid, comparable to NMN-based SERS substrates. The enhanced SERS activity resulted from a double-defect mechanism introduced by Sr doping, involving surface oxygen vacancies and Ti<sup>3+</sup> defect energy levels. These defects worked synergistically to create a multichannel CT pathway that significantly amplified the SERS performance. XPS analysis confirmed Ti<sup>3+</sup> states and oxygen vacancies, while EIS measurements demonstrated improved charge transfer in Sr-doped samples, directly correlating with enhanced SERS activity. Interestingly, Jiang *et al.*<sup>63</sup> investigated the SERS activity of Nd-doped MoS<sub>2</sub> nanoflowers (NFs) and found that 2% Nd-doped MoS<sub>2</sub> exhibited remarkable SERS activity with an EF of approximately  $1.29 \times 10^6$  towards MB analyte, attributed to the energy level transition and CT mechanism. The effectiveness of this SERS substrate was again demonstrated through its ability to detect various compounds at extremely low concentrations, achieving limits of detection of  $10^{-8}$  M for bilirubin and  $10^{-9}$  M for both dipterex and bisphenol A. Their XPS and PL studies confirmed the chemical enhancement mechanism through charge transfer, with XPS detecting binding energy changes and PL verifying Nd<sup>3+</sup>-

associated energy level transitions. Similarly, Adesoye *et al.*<sup>64</sup> investigated SERS enhancement using 5,5-dithiobis-2-nitrobenzoic acid (DTNB) as a model compound with ZnO and Mg-doped ZnO substrates. It was found that 2% Mg-doped ZnO showed the highest SERS enhancement, producing a signal approximately three times stronger than pure DTNB, while pure ZnO showed less than twice SERS enhancement. The improved performance was attributed to bandgap suppression and the creation of new surface-state energy levels through Mg doping, which facilitated CT between the VB of ZnO and the LUMO of DTNB. Furthermore, Zhao *et al.*<sup>65</sup> and Ji *et al.*<sup>44</sup> investigated the enhancement of SERS performance by Nd-doping in TiO<sub>2</sub> and Zn-ion doping in ZrO<sub>2</sub> nanoparticles (NPs), respectively, achieving excellent sensitivity.

Similarly, doped semiconductors are also shown to enhance SERS detection capabilities through multiple mechanisms<sup>66,67</sup> *i.e.* through heterojunctions and interface formation between two different semiconductors resulting in improved charge separation. In SERS, such heterojunctions/interfaces are responsible for amplifying the Raman signals for detecting low-concentration of molecules, while in photocatalysis, reduction in charge recombination is promoted along with light absorption, boosting the efficiency in pollutant degradation and energy conversion. These properties make heterojunctions ideal for high-performance SERS sensors and photocatalysts. Recently, Yang *et al.*<sup>9</sup> fabricated a Cu<sub>2</sub>O/g-C<sub>3</sub>N<sub>4</sub>-based p-n heterojunction (MPH) device, integrating SERS detection with photocatalytic degradation, as shown in scanning electron microscopy (SEM) micrographs (Fig. 3(d)), demonstrating that Cu<sub>2</sub>O microspheres successfully couple with g-C<sub>3</sub>N<sub>4</sub> while retaining their original structure. The high-resolution transmission electron microscopy (HRTEM) image (Fig. 3(e)) shows the lattice fringes with an interplanar spacing of 0.24 nm, corresponding to the (111) plane of Cu<sub>2</sub>O microspheres. The Cu<sub>2</sub>O/g-C<sub>3</sub>N<sub>4</sub>-0.2 MPH device (with 20% g-C<sub>3</sub>N<sub>4</sub>) exhibited enhanced charge separation, high SERS sensitivity with an EF of  $2.43 \times 10^6$ , and 98.3% methyl orange (MO) degradation efficiency under visible light. The device maintained over 93% photocatalytic efficiency after 216 days, with stable structural performance, as further confirmed by XRD and SEM results shown in Fig. 3(f and g). The Z-type mechanism of the device contributed to its high self-cleaning capability and efficient pollutant detection.<sup>9</sup>

Recent studies have shown that 2D materials like MoS<sub>2</sub>, GO, and reduced GO (rGO) can serve as effective SERS substrates and photocatalysts without the need for EM enhancement or heterojunction formation. These materials offer tunable band structures, abundant surface-active sites, and strong light-matter interactions, enabling efficient CT-induced Raman enhancement and visible-light-driven photocatalysis. Our group has demonstrated that GO<sup>68</sup> and doped GO,<sup>69</sup> synthesized *via* a modified Hummers' method, exhibits high photocatalytic activity and excellent adsorption capacity, while 1T/2H phase-engineered MoS<sub>2</sub> nanosheets show improved photocatalysis due to enhanced charge separation.<sup>70</sup> In one study, MoS<sub>2</sub> nanosheets with tunable defects exhibited a low detection limit for SERS,<sup>35</sup> while in another, 3D hollow-structured MoS<sub>2</sub>





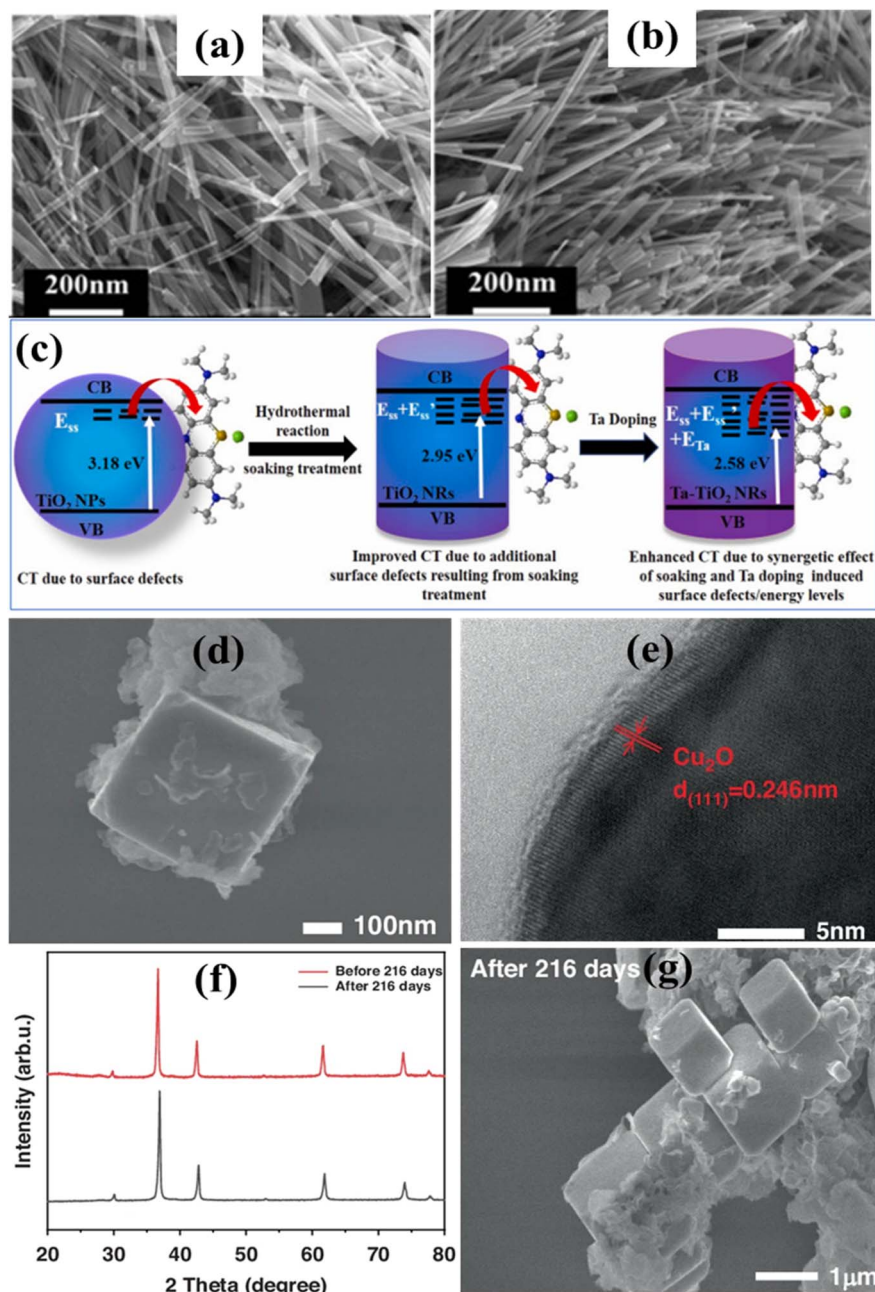


Fig. 3 (a and b) SEM images of TiO<sub>2</sub> and Ta-doped-TiO<sub>2</sub> NRs. (c) Schematic of various CT processes for enhanced SERS activities attributed to the hydrothermal synthesis process of TiO<sub>2</sub> NRs followed by soaking treatment and Ta doping, indicating the generation of various defects/energy levels (reprinted with permission from ref. 27. Copyright 2022, Elsevier). (d and e) SEM and HRTEM images of Cu<sub>2</sub>O/g-C<sub>3</sub>N<sub>4</sub> MPH, respectively. (f and g) XRD patterns of Cu<sub>2</sub>O/g-C<sub>3</sub>N<sub>4</sub>-0.2 MPH 216 days pre- and post-photocatalysis and SEM image of Cu<sub>2</sub>O/g-C<sub>3</sub>N<sub>4</sub>-0.2 MPH 216 days post-photocatalysis (reprinted from open source access ref. 9).

achieved significant enhancement for rhodamine 6G detection.<sup>71</sup> These findings highlight the potential of metal-free 2D materials as sustainable, multifunctional platforms for both SERS sensing and pollutant removal.

Thus, the introduction of dopants and formation of heterojunctions in sole/hybrid semiconductors can improve the CT efficiency, modify band structures, and creates beneficial defect states that contribute to SERS enhancement. These advances suggest that doped and heterojunction/hybrid semiconductor SERS substrates could provide a cost-effective and efficient

alternative to noble metal-based systems while offering additional advantages such as tunable optical and electronic properties for potential applications.

### 3.2 Through interface coupling of semiconductor nano-photocatalysts with NMNs

The development of SERS substrates through the interface coupling of nano-photocatalysts with NMNs represents a significant breakthrough, improving the sensitivity, stability,



and multifunctionality of such hybrid SERSB substrates. At the heart of this innovation lies the unique optical properties of NMNs, specifically LSPR,<sup>51,72</sup> responsible for EM SERS enhancement. NMNs generate strong LSPR when exposed to specific wavelengths of light, which create intense localized EM fields around the NMNs, resulting in the formation of “hot-spots” between the NMNs where the EM field is dramatically amplified.<sup>73</sup> This amplification plays a critical role in enhancing the Raman signals of molecules adsorbed within the ‘hot spot’ or close to the NMN surface, enabling the detection of low-concentration analytes.<sup>74</sup> Interestingly, when NMNs are coupled with semiconductor nano-photocatalysts, the resulting composite materials can simultaneously leverage both the EM and CT SERS enhancement provided by NMNs and photocatalysts, respectively. This coupling not only amplifies the Raman signals from the target molecules but also facilitates the generation of energetic hot electrons through plasmon decay. These hot electrons can drive chemical reactions, boosting the efficiency of the SERS process.<sup>75</sup> Additionally, surface functionalities such as the surface area or surface defects of the substrate enhances the adsorption of analytes on its surface increasing their effective concentration near the hotspots due to NMNs and thereby further enhancing the SERS signals.<sup>27</sup> This synergy between plasmonic (*i.e.* NMNs) and semiconductor photocatalysts with enhanced surface area/properties also increases the selectivity of the substrate for specific analytes.<sup>76</sup>

Moreover, the interface coupling enables CT processes between the NMNs and the nano-photocatalyst. The tunability of plasmonic resonance through structural modifications allows the substrate to be optimized for specific wavelengths of excitation light, offering enhanced flexibility for different applications.<sup>77</sup> The combined EM and CT SERS enhancement mechanisms significantly boost the overall efficiency of the SERS process, providing a robust platform for advanced analytical applications. Pramanick *et al.*<sup>78</sup> studied Cu and Ag NPs and their CuAg<sub>2</sub> nanocomposites at varying ratios for photocatalytic degradation of pollutants under visible light. The Ag-rich nanocomposite (CuAg<sub>2</sub>) exhibited the highest photocatalytic activity, primarily due to its enhanced light-harvesting ability and synergistic CT between Cu and Ag. CuAg<sub>2</sub> effectively mineralized pharmaceutical pollutants, including sulfamethoxazole (SMX) and norfloxacin (NOR). In addition, CuAg<sub>2</sub> also served as a SERS substrate for detecting these pollutants. An *operando* catalytic activity study and liquid chromatography-mass spectrometry (LC-MS) were employed to investigate the degradation pathways for SMX and NOR using the SERS mechanism, further elucidating the photocatalytic process discussed in Section 2.3.<sup>78</sup>

Thermoelectric materials, like gallium nitride (GaN), are gaining attention for their dual role as photocatalysts and SERS enhancers. For example, Tan *et al.*<sup>79</sup> designed an electric-field-induced SERS (E-SERS) substrate by combining GaN with Ag NPs, achieving a tenfold enhancement in SERS signals over conventional noble metal substrates. The thermoelectric potential of GaN modulates CT by shifting the Fermi level of Ag, increasing electron transition rates, especially for low-Raman-scattering molecules. This platform also enables plasmon-

driven redox reaction monitoring. Finite element analysis clarified the mechanisms: in n-type GaN, CT from GaN to Ag forms a Schottky barrier (Fig. 4(a-c)). Heating generates a negative thermoelectric potential, raising GaN's bands and enhancing the electron flow to Ag, activating O<sub>2</sub> and oxidizing *p*-aminothiophenol (PATP) to dimethylaminoborane (DMAB), while cooling reverses this with a positive potential, lowering the barrier and allowing hot electrons to flow from Ag to GaN, enabling resonant back-conversion of DMAB to PATP.<sup>79</sup>

Similarly, a combination of 2D materials with NMNs has garnered significant attention for SERS applications, as these materials can offer unique properties such as large surface areas, tunable electronic structures, and strong plasmonic effects. For example, Rahim *et al.*<sup>7</sup> presents an ultrasensitive SERS platform based on a 2,3,5,6-tetrafluorotetracyanoquinodimethane (F4TCNQ)/MoS<sub>2</sub> heterostructure grown on anodic aluminum oxide (AAO) templates and flat Al<sub>2</sub>O<sub>3</sub>. The optimized heterostructure showed the highest SERS enhancement due to the strong coupling between EM and CT mechanisms. This dual enhancement operates *via* two complementary pathways: charge transfer between probe molecules and the heterostructure amplifying Raman signals through chemical mechanisms, while intense localized electric fields within V-shaped nanocavities enhance light-matter interactions through electromagnetic effects. Comprehensive characterization employed ultraviolet photoelectron spectroscopy to probe the electronic structures and confirm the charge transfer processes, while COMSOL simulations mapped electric field distributions within nanocavities to identify regions of electromagnetic enhancement. These analytical approaches provided a thorough mechanistic understanding of the SERS processes. The heterostructure enhanced photo-induced CT, achieving an ultralow limit of detection (LOD) of  $9.0 \times 10^{-16}$  M and a high EF, rivaling noble metal substrates. The SERS stability up to 3 months with a rapid SERS response was observed. Additionally, the platform demonstrated effective photodegradation of MB, with hydrophilic Al<sub>2</sub>O<sub>3</sub> surfaces showing faster degradation (84%) than AAO (79%). The substrate also enabled sensitive detection of Hg<sup>2+</sup> ions in water with an LOD of  $10^{-11}$  M. Overall, the combination of nano-architecture templates and organic/inorganic heterostructures offers high sensitivity, stability, and versatility for SERS sensing.<sup>7</sup>

Similarly, magnetic plasmonic photocatalysts are advanced materials that combine the unique properties of magnetic, plasmonic, and photocatalytic components to create SERS platforms for various environmental applications. For example, Liao *et al.*<sup>80</sup> developed Fe<sub>3</sub>O<sub>4</sub>@mTiO<sub>2</sub>@Ag@GO through a green, microwave-assisted hydrothermal process, as shown by the HRTEM image in Fig. 4(d). UV-vis spectra shown in Fig. 4(e) further verified the successful formation of Ag NPs in the composite, resulting in characteristic LSPR peaks at 338 and 414 nm and exhibited enhanced light absorption in the 350–450 nm range. This is due to the combined LSPR effect of Ag NPs and intrinsic absorption of the TiO<sub>2</sub> shell. The resulting material was investigated for SERS detection and photocatalytic degradation of fluoroquinolone – NOR, ciprofloxacin (CIP), and





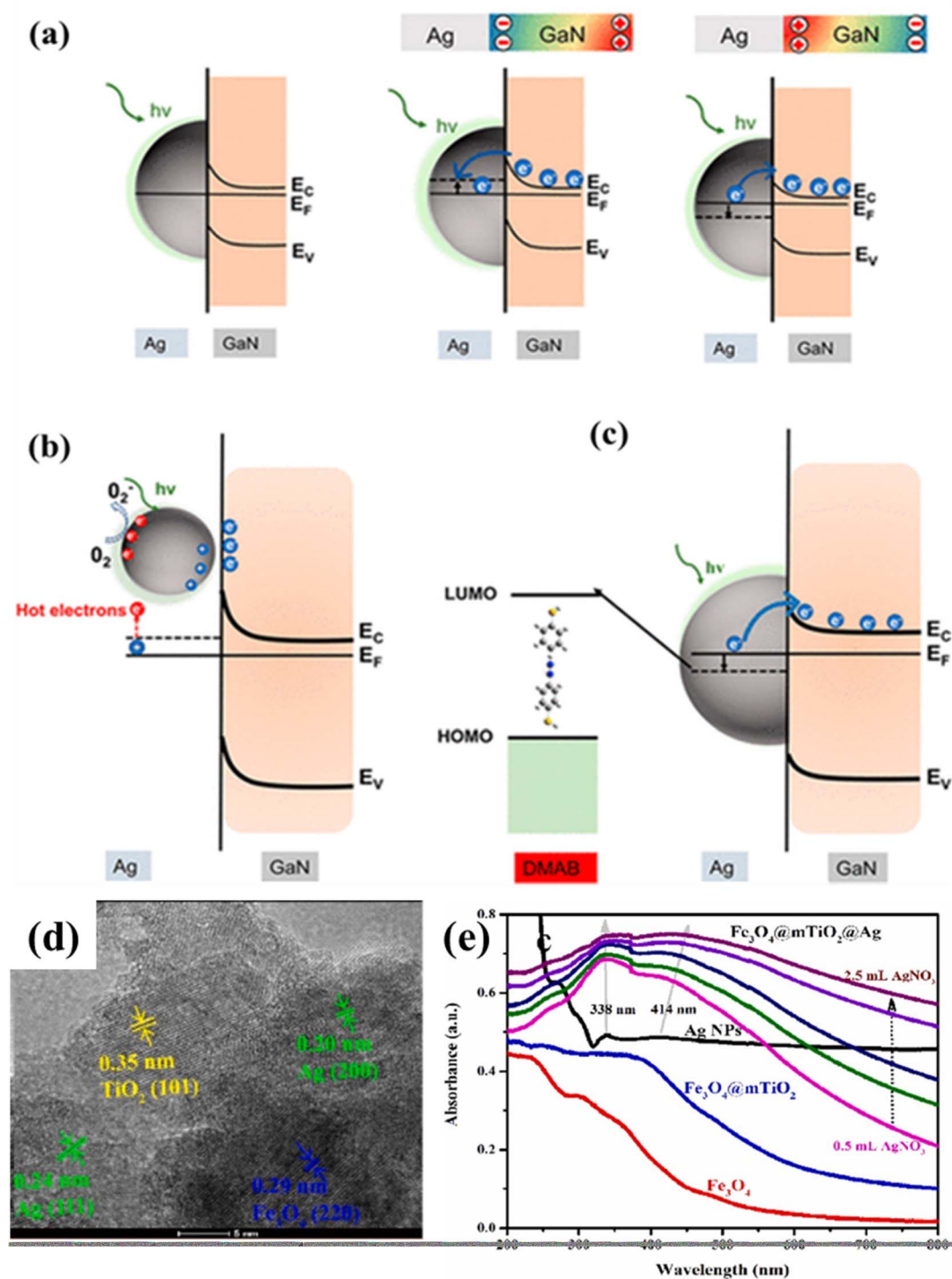


Fig. 4 (a–c) The energy band diagram and the direction of CT in the Ag–GaN structure at room temperature, as well as during the heating and cooling processes (reprinted with permission from ref. 79. Copyright 2023, American Chemical Society). (d) HRTEM image and (e) absorption spectra of  $\text{Fe}_3\text{O}_4@\text{mTiO}_2@\text{Ag}@GO$  (reprinted with permission from ref. 80. Copyright 2025, Elsevier).

enrofloxacin (ENR) with an LOD as low as  $0.1 \mu\text{g mL}^{-1}$ , supported by density functional theory (DFT) calculations. The photocatalytic degradation of NOR was 4.6 and 1.4 times faster on  $\text{Fe}_3\text{O}_4@\text{mTiO}_2@\text{Ag}@GO$  than on  $\text{Fe}_3\text{O}_4@\text{mTiO}_2$  and  $\text{Fe}_3\text{O}_4@\text{mTiO}_2@\text{Ag}$ , respectively. The composite material was also recyclable for at least five cycles.<sup>80</sup>

Overall, interface coupling of photocatalysts with NMNs creates a powerful platform for SERS applications, merging the analytical capabilities of SERS with the reactive versatility of photocatalysis. This innovative approach not only addresses the limitations of traditional SERS substrates but also opens up new avenues for the detection and degradation of hazardous



chemicals, making these hybrid systems highly suitable for long-term use in diverse fields.

### 3.3 Through *in situ* SERS monitoring of photocatalytic reaction mechanisms

*In situ* SERS monitoring of photocatalytic reactions has emerged as a pivotal technique for understanding reaction mechanisms at the molecular level. This approach supports the unique properties of SERS substrates, particularly those that are also effective photocatalysts, to provide real-time insights on how materials behave under working conditions in photocatalytic processes.<sup>81</sup> As discussed earlier, these materials primarily fall into two categories: hybrid nanostructures composed of semiconductors, either with or without NMNs.

Various SERS substrates, including NMNs and metal-organic frameworks, have been utilized to monitor photocatalytic reactions, allowing for the observation of charge carrier dynamics and reaction pathways. *In situ* SERS enables the tracking of dynamic changes during photocatalytic reactions, providing direct evidence of intermediate states and electron transfer mechanisms, as shown in Fig. 5(a).<sup>82</sup> For example, Zhang *et al.*<sup>82</sup> explored *in situ* photocatalytic degradation of 4-chlorophenol (4-CP) using TiO<sub>2</sub>@Ag/cellulose microfibers as both a photocatalyst and an SERS substrate, as depicted in Fig. 5(b). The study provided insights into the degradation pathway through time-resolved SERS analysis. Time-resolved SERS spectra during the photodegradation process are shown in Fig. 5(c), with several snapshot spectra at different stages, highlighted in Fig. 5(d). In the first minute of the photocatalytic reaction, the SERS peak at 1048 cm<sup>-1</sup> (C–Cl stretching) disappeared, while peaks for O–H and C–O stretching shifted, indicating the formation of hydroquinone (HQ) *via* dichlorination and hydroxylation. Over time, HQ was further oxidized to 1,4-benzoquinone (BQ), as evidenced by the appearance of SERS peaks for C–O stretching (1605 cm<sup>-1</sup>) and C–H in-plane bending (1163 cm<sup>-1</sup>). After 4 minutes, the SERS intensities of multiple peaks related to aromatic compounds were enhanced, suggesting the formation of quinhydrone. By 8 minutes, a sharp decrease in SERS peak intensities indicated the cleavage of the aromatic ring. The intensity ratio between 1605 cm<sup>-1</sup> and 1575 cm<sup>-1</sup> was used to track the generation and conversion of quinhydrone, revealing that it was the final aromatic intermediate before ring cleavage, as shown in Fig. 5(e). This work demonstrated the power of time-resolved SERS as a sensitive and molecular fingerprinting tool for monitoring photocatalytic molecular transformations and intermediate species in real time.

As discussed in Section 2.2, CuAg<sub>2</sub> exhibited dual functionality as a photocatalyst and an SERS-active material. *Operando* SERS monitoring revealed real-time degradation of *p*-nitrophenol, with the –NO<sub>2</sub> peak at 1290 cm<sup>-1</sup> decreasing over time, indicating its conversion to aminophenol. SMX showed complete loss of Raman signals within 45 minutes, while NOR exhibited a gradual decline of the 1380 cm<sup>-1</sup> band, confirming its degradation. These results demonstrate the effectiveness of *operando* SERS in tracking photocatalytic reactions and

intermediate species.<sup>78</sup> In addition, Jiang *et al.*<sup>83</sup> introduced a flexible cotton fabric (Cot) Cot/3% Ca–TiO<sub>2</sub> substrate exhibiting high SERS activity and stability, which was used for the rapid *in situ* detection of quinolone antibiotics (like enrofloxacin) in aquatic products and natural water systems. The detection process involved wiping samples from surfaces (*e.g.*, fish) and analyzing those using SERS, achieving low LODs of 10<sup>-9</sup> M. The minimum detectable concentrations of the three antibiotic residues in real water samples reached as low as 1 × 10<sup>-8</sup> M. The calculated LODs for the three antibiotics were 8.41 × 10<sup>-9</sup> M, 9.89 × 10<sup>-9</sup> M, and 9.54 × 10<sup>-9</sup> M, respectively. Interestingly, Ag triangular nanoplate (AgTNP)-based AgTNP@TiO<sub>2</sub>@Ag core-satellite composites represented a significant advancement in sensitive sensing and *in situ* SERS monitoring of organic dye photodegradation using portable Raman spectroscopy. These composites capitalized on the unique properties of AgTNPs and TiO<sub>2</sub> to generate abundant hot spots, significantly enhancing SERS sensitivity. This advancement enabled the precise detection of MB dyes at extremely low concentrations, with a remarkable sensitivity reaching 10<sup>-10</sup> M.<sup>84</sup> Similarly, Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub>-Au NPs have demonstrated superior photocatalytic performance due to their reduced bandgap energy and LSPR from Au NPs. Compared to Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub>, which showed minimal changes in MO SERS spectra, Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub>-Au NPs achieved a significantly higher degradation rate, reducing the MO concentration by 88.4% in just 32 minutes, compared to 3.7% for Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub>.<sup>85</sup> Similarly, Ag@AgX on a polyaniline (PANI) surface enabled strong SERS detection. The Fe<sub>3</sub>O<sub>4</sub>@C/1D PANI/Ag@AgCl photocatalyst effectively detected rhodamine B and monitored its degradation in real time serving as both a photocatalyst and an SERS substrate.<sup>86</sup>

Theoretical studies on SERS have been performed to understand the EM and CM mechanisms. Additionally, the finite-difference time-domain (FDTD) simulations and DFT models help in optimizing nanostructure designs and predicting their SERS performances. Similarly, 2D correlation spectroscopy (2D-COS) combined with SERS provides insights into CT mechanisms, improving the understanding of hybrid materials for enhanced SERS and photocatalysis. For example, Chu *et al.*<sup>87</sup> fabricated a 3D Ag@ZnSe(*x*) structure by sputtering Ag and ZnSe onto a polystyrene template, which introduced a CT effect within the system, as was validated through 2D-COS-SERS. The photodegradation of malachite green (MG) was catalyzed by the CT effect, and it was successfully monitored by *in situ* using SERS. Notably, the degree of catalytic degradation by Ag@ZnSe(*x*) was proportional to the extent of CT ( $\rho_{CT}$ ). Both the SERS and catalytic mechanisms were thoroughly analyzed using the 2D-COS-SERS technique. This study highlights the synergistic effects of EM and CT mechanisms offering new insights into photocatalysis with dye molecules and real-time monitoring of catalytic processes.

Such advancements in synergetic nanomaterials combining photocatalytic and SERS activity have revolutionized *in situ* monitoring of photocatalytic processes and understanding of the proper mechanisms. These innovative SERS materials/substrates not only provide unparalleled sensitivity and real-



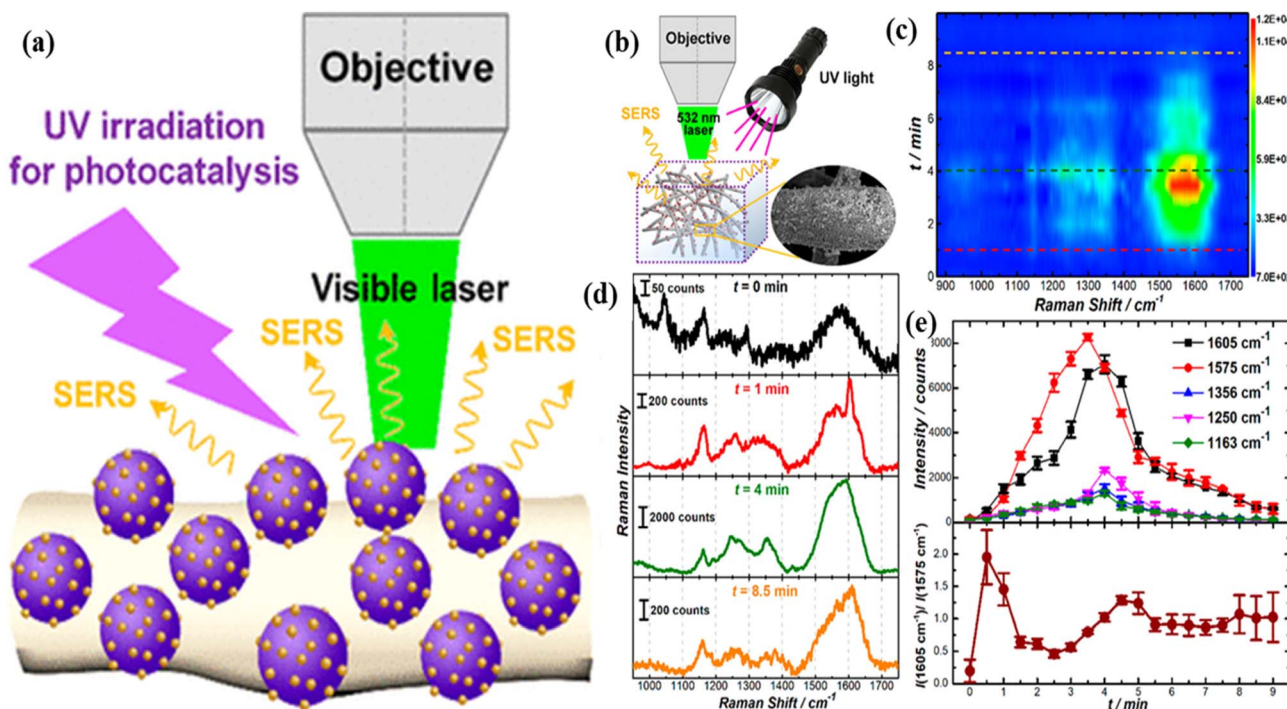


Fig. 5 (a) Schematic showing *in situ* SERS detection and on-site photocatalytic degradation. (b) A schematic diagram illustrating the *in situ* reaction monitoring using SERS. (c) The temporal progression of SERS spectra during the photocatalytic degradation of 4-CP on TiO<sub>2</sub>@Ag/CMFs. (d) Snapshot SERS spectra captured at reaction times of 0, 1, 4, and 8.5 minutes. (e) Temporal changes in the (upper panel) SERS peak intensities of Raman modes at 1605, 1575, 1356, 1250, and 1163 cm<sup>-1</sup> and (bottom panel) the intensity ratio between the 1605 cm<sup>-1</sup> and 1575 cm<sup>-1</sup> modes throughout the photocatalytic reaction (reprinted with permission from ref. 82. Copyright 2018, American Chemical Society).

time insights into reaction mechanisms but also hold immense potential for environmental monitoring and pollution control, making them invaluable tools for addressing global environmental challenges.

### 3.4 Through designing recyclable SERS substrates and protective coating for long term sustainable applications

Designing recyclable SERS substrates and protective coatings for long-term applications involves innovative materials and fabrication strategies aimed at enhancing both Raman signal performance, structural stability of the materials and operational durability. Recent research has focused on the development of metal–semiconductor based hybrid nanostructures that not only deliver strong Raman signal enhancement but also offer recyclability and robustness under varying environmental conditions. In this context, our group recently developed ZnO/Ag nanohybrid substrates that exhibit outstanding sensitivity, stability, and recyclability, using MB as a model pollutant. These substrates achieved a high EF of  $3.7 \times 10^7$  and an ultralow detection limit of  $10^{-12}$  M, underscoring their suitability for environmental monitoring and analytical applications. The synergistic combination of Ag nanocrystals (which generate intense LSPR) and the chemically stable ZnO matrix contributes to the long-term functional integrity of the hybrid system. Impressively, the substrates retained over 89% of their initial SERS performance after four cycles of UV-induced self-cleaning, confirming their efficient photodegradation capability and excellent reusability.

Similarly, Korcoban *et al.*<sup>88</sup> developed a recyclable SERS sensor using colloidal lithography, forming TiO<sub>2</sub> hollow-shell structures decorated with Ag NPs. Optimal Ag NP deposition achieved high SERS sensitivity, supported at least three detect/clean cycles, and maintained reproducibility across 30 tests. Excessive Ag reduced the photocatalytic efficiency, highlighting the importance of precise metal loading. This approach offers a tunable platform for integrating SERS and self-cleaning in environmental applications. Building on this, another study presented a simple and green method for preparing Au NR-based Au NRs@TiO<sub>2</sub> nanocomposites, where the TiO<sub>2</sub> shell was formed *via in situ* reduction at room temperature. These nanocomposites demonstrated superior SERS activity compared to pure Au NRs, offering enhanced sensitivity and reproducibility for pollutant detection. The Au NRs@TiO<sub>2</sub> substrates also exhibited notable recyclability, with the ability to self-clean *via* UV light, maintaining their SERS performance after multiple cycles.<sup>89</sup> This combination of high sensitivity, reusability, and portability underscores the potential for using these materials in real-world environmental monitoring, where complex samples and rapid detection are often required. In addition, several other studies on noble metal/metal oxide hybrids have explored similar structures and approaches, further advancing the development of recyclable and high-performance SERS substrates.<sup>11,90–92</sup>

To further enhance both sensitivity and recyclability in SERS applications, researchers have explored composites that integrate traditional metal oxide photocatalysts and emerging

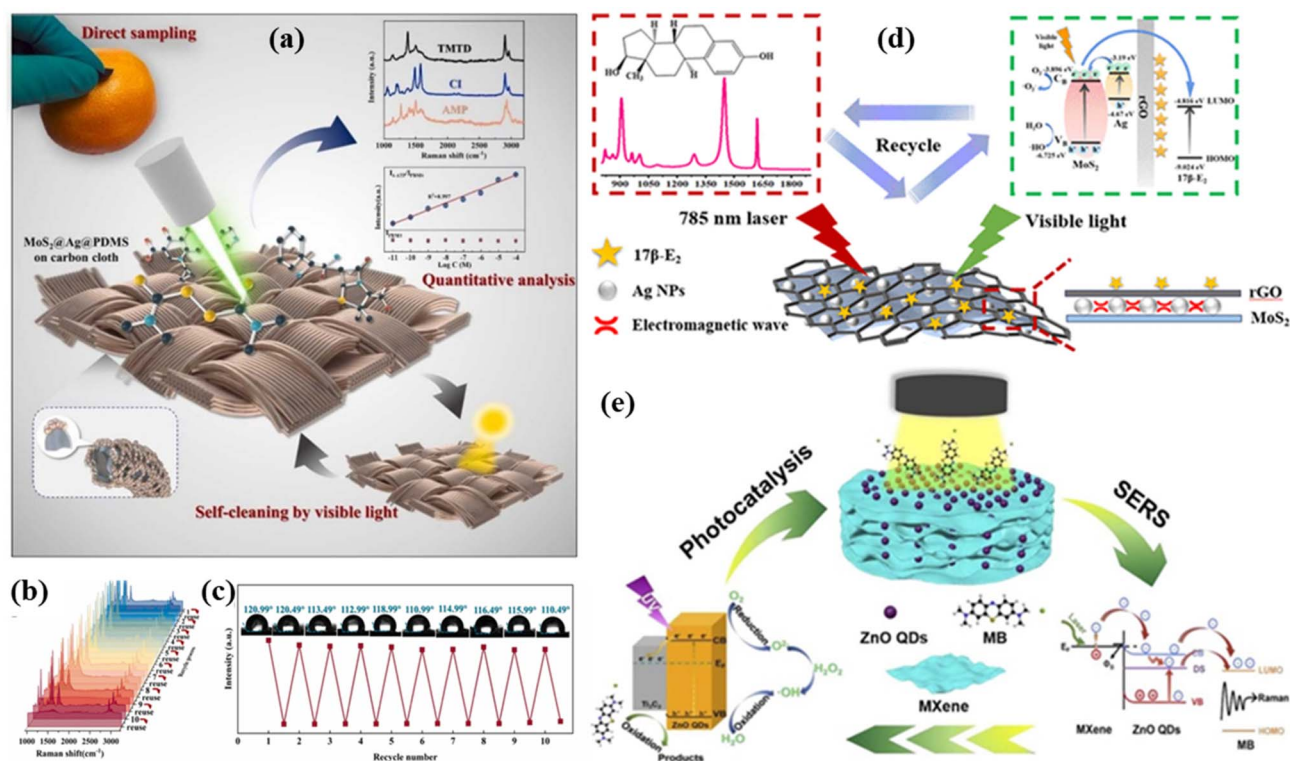




functional nanomaterials with excellent features including photocatalytic properties like 2D materials, NMNs, *etc.* These multifunctional platforms harness the plasmonic effects of NMNs, *i.e.* Ag or Au, the CT capabilities of 2D materials, and the photocatalytic/self-cleaning functions of metal oxide photocatalysts, making them highly adaptable to real-world sensing challenges. A notable example is the hybrid SERS substrate composed of carbon cloth (CC), MoS<sub>2</sub>, Ag NPs, and polydimethylsiloxane (PDMS), *i.e.* CC/MoS<sub>2</sub>@Ag@PDMS, to create a highly stable and flexible material, as produced by Song *et al.*<sup>93</sup> (Fig. 6(a)). It maintained performance over 100 deformation cycles and showed a high EF  $\sim 10^7$  with a detection limit of  $10^{-12}$  M for 4-ATP ( $R^2 = 0.997$ ). The substrate benefits from both EM and CM effects and features MoS<sub>2</sub>-based self-cleaning, enabling easy reuse—ideal for point-of-care testing and field applications (Fig. 6(b and c)). Similarly, Barveen *et al.*<sup>94</sup> developed a reusable, flexible SERS substrate by anchoring Au NPs onto MoS<sub>2</sub> grown on CC *via* photoreduction. It achieved a detection limit of  $10^{-11}$  M for nitrofurantoin, combining EM enhancement from Au and CT from MoS<sub>2</sub>. The substrate remained stable after 50 bends, enabled swab-based detection on irregular surfaces, and featured UVC-assisted self-cleaning for multiple reuse cycles, highlighting its potential in food safety applications. Additionally, Fang *et al.*<sup>95</sup> fabricated a self-cleaning, recyclable SERS substrate based on AuNPs/TiO<sub>2</sub>/

Ti<sub>3</sub>C<sub>2</sub> heterostructures for MG pollutant detection. The substrate demonstrated excellent photocatalytic activity, enabling effective self-cleaning under light irradiation. It retained its SERS performance over five reuse cycles, even in complex food matrices, displaying strong potential for sustainable and practical applications in food safety monitoring.

Expanding the range of analytes detected using SERS, a composite based on Ag NPs, MoS<sub>2</sub>, and reduced rGO was developed by Liu *et al.*<sup>96</sup> for the trace detection of 17 $\beta$ -estradiol (17 $\beta$ -E2) in environmental water. 17 $\beta$ -E2 is a common estrogenic steroid used in animal husbandry that can contaminate water sources due to its widespread abuse. This composite material exhibited a high SERS, EF of  $1.95 \times 10^7$  and a low LOD of  $5 \times 10^{-12}$  M, providing excellent sensitivity for 17 $\beta$ -E2 detection. The rGO layer not only provided a protective coating for the Ag NPs, preventing oxidation, but also facilitated the adsorption of the target molecule, thus enhancing the SERS signal (Fig. 6(d)). The material demonstrated a strong linear relationship ( $R^2 = 0.994$ ), good stability (RSD = 4.74%), and excellent anti-interference ability, with recovery rates of 100.15–108.00% for 17 $\beta$ -E2 in farm wastewater samples. These results suggest that the composite is potential for detecting endocrine-disrupting chemicals in environmental monitoring applications.



**Fig. 6** (a) Flexible CC/MoS<sub>2</sub>@Ag@PDMS substrate designed for self-cleaning and highly sensitive quantitative point-of-care testing of antibiotics and pesticides. (b) SERS spectra of  $1.0 \times 10^{-6}$  M 4-ATP collected during cyclic photocatalysis on CC/MoS<sub>2</sub>@Ag@PDMS substrates. (c) The intensity of the 4-ATP characteristic peak at  $1428 \text{ cm}^{-1}$  and the variation in the contact angle on the surface of the composite flexible substrate after multiple detection cycles (reprinted with permission from ref. 93. Copyright 2023, Elsevier). (d) SERS detection and the photocatalytic degradation of 17 $\beta$ -E2 by MoS<sub>2</sub>/Ag@rGO (reprinted with permission.<sup>96</sup> Copyright 2024, American Chemical Society). (e) Schematic illustration of the recyclable SERS mechanism of the Ti<sub>3</sub>C<sub>2</sub>/ZnO-80 film (reprinted with permission from ref. 97. Copyright 2025, Elsevier).



Table 1 List of most promising semiconductor-based SERS substrates reported over the past 2–3 years

| Sr. no. | Material   | Synthesis method  | SERS mechanism | Enhancement factor                              | Analyte detected                                  | Ref. |
|---------|--|---|----------------|---|---|------|
| 1       | WO <sub>3-x</sub> /TiO <sub>2</sub> nanocomposite      | Solvothermal + thermal reduction  | CM-dominant    | $1.2 \times 10^5$                               | R6G   | 98   |
| 2       | TiO <sub>2</sub> aerogels                              | Sol-gel + supercritical drying  | CM-dominant    | $10^5$  | 4-Mercaptobenzoic acid                            | 99   |
| 3       | TiO <sub>2</sub> multi-leg nanotubes                   | Electrochemical anodization   | CM + weak EM   | $10^4$  | MB  | 100  |
| 4       | MXene films  | Chemical etching method   | CM dominant    | $3.27 \times 10^{12}$                           | R6G   | 101  |
| 5       | Au/ZnO   | Hydrothermal method + microwave radiation + photodeposition   | EM             | $10^6$  | R6G   | 102  |
| 6       | Ag/TiO <sub>2</sub>                                    | Chemical vapour deposition  | EM             | —   | RhB   | 88   |
| 7       | Au/TiO <sub>2</sub>                                    | Binary surfactant-assisted seed-mediated method   | EM + CM        | —   | R6G, malachite green (MG) and crystal violet (CV) | 103  |
| 8       | MoS <sub>2</sub>                                       | Hydrothermal method   | EM + CM        | $10^9$  | Nitrofurantoin                                    | 94   |
| 9       | AuNPs/TiO <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> | Oxidation of Ti <sub>3</sub> C <sub>2</sub> + alkali phase transformation + AuNPs deposition (chemical reduction)     | EM + CM        | $6.51 \times 10^5$ (MG) $2.67 \times 10^6$ (CV) | MG and CV   | 95   |
| 10      | g-C <sub>3</sub> N <sub>4</sub> /Au/Ag                 | E-beam evaporation (Ag NRs) + organic interface self-assembly (Au NPs) + g-C <sub>3</sub> N <sub>4</sub> drop coating | EM dominant    | $10^7$  | Bisphenol   | 104  |

Table 1 presents recent semiconductor-based SERS substrates with their synthesis methods, SERS mechanisms and enhancement factors, demonstrating their effectiveness in sensitive molecular detection. In addition, several other studies have reported similar hybrid systems that leverage the synergistic effects of metal oxides, 2D materials, and noble metals, further confirming the broad potential of these composites in enhancing SERS performance and ensuring reusability across various applications.<sup>8,92,104–108</sup> Recent advancements in SERS have led to the development of noble metal-free substrates for recyclable and flexible SERS sensors. Liu *et al.*<sup>97</sup> introduced a Ti<sub>3</sub>C<sub>2</sub> MXene/ZnO quantum dots (Ti<sub>3</sub>C<sub>2</sub>/ZnO) heterostructure film, fabricated using a vacuum-assisted filtration technique, offering remarkable flexibility and high sensitivity. The sensor exhibited excellent CT efficiency due to oxygen vacancies in the ZnO quantum dots and the Schottky barrier between Ti<sub>3</sub>C<sub>2</sub> and ZnO, resulting in a low detection limit of  $1 \times 10^{-7}$  M for 4-mercaptopyridine (4-MPY) molecules. It demonstrated uniform and stable signals, maintaining performance for 60 days at room temperature with an RSD of 10.7%. Moreover, the substrate showed photocatalytic self-cleaning abilities, successfully degrading MB residues and achieving high reusability, as shown in Fig. 6(e). This noble metal-free, flexible, and recyclable SERS sensor holds significant potential for *in situ* molecular detection in food safety and environmental monitoring due to its high performance, sustainability, and low cost. These developments demonstrate the promising potential of recyclable and self-cleaning SERS substrates for real-world applications in food safety, environmental protection, and surface contaminant detection.

## 4. Outlook and summary

Semiconductor-based nano-photocatalysts are rapidly transforming the design of SERS substrates by overcoming key limitations of traditional noble metal (*i.e.* NMN) systems. Their unique properties—including CT, photocatalytic self-cleaning, and efficient surface adsorption—enhance the SERS sensitivity as well as the durability and reusability of SERS materials/substrates. The hybrid architectures that integrate various semiconductors with plasmonic metals offer synergistic EM and CM enhancement mechanisms, making them particularly valuable for real-time monitoring of photocatalytic reactions, intermediate species, and surface dynamics. These platforms have shown tremendous promise in environmental sensing, biomedical diagnostics, and energy-related applications.

The future of SERS in catalysis and energy conversion holds vast potential, with several emerging directions shaping its evolution:

**Operando and *in situ* SERS:** the shift from model systems to complex, real-world catalytic environments under true *operando* conditions—including gas-phase and high-temperature reactions—is a major milestone. Real-time tracking of chemical transformations will deepen our understanding of active sites, kinetics, and mechanistic pathways.

**Smart and multifunctional hybrid substrates:** advances in combining plasmonic nanostructures with 2D materials,



magnetic/thermoelectric semiconductors, and flexible supports are enhancing both the SERS response and photocatalytic efficiency. Self-cleaning, recyclable designs offer sustainability and longevity for repeated use.

Integration with machine learning and spectral analysis: the inherent complexity and high sensitivity of SERS data can lead to challenges in interpreting spectra. Emerging AI-powered tools are showing promise in spectral deconvolution and accurate identification of molecular species, helping translate SERS into robust, automated sensing platforms.

Single-molecule and single-atom catalysis: the use of SERS for probing single-molecule reactivity and single-atom catalysts is opening new frontiers in nanoscale catalysis and energy research, allowing unprecedented insights into catalytic behavior at the atomic level.

Transitioning from research to industry: to make SERS viable for industrial catalysis, systems must be operable under practical conditions, beyond ideal lab setups. Scalable fabrication methods, stability under harsh environments, and robust substrate reusability will be critical in bridging this gap.

In summary, SERS is no longer just a common analytical technique—it is evolving into a multifunctional, *operando*-compatible tool with broad relevance across sustainable catalysis, energy conversion, and smart sensing. Continued innovation in hybrid material design, data-driven interpretation, and scalable device fabrication will be pivotal to realizing the full industrial and environmental potential of SERS in the decades ahead.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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