

Robust and recyclable photo-induced enhanced Raman scattering platform based on ZnO thin film decorated with Au nanoparticles for trace analyte detection

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ABSTRACT

In this study, we present an efficient method for fabricating surface-enhanced Raman scattering (SERS) substrates using ZnO@Au thin films, achieved through radio frequency magnetron sputtering followed by post-annealing process. The photo-induced enhanced Raman scattering (PIERS) effect was thoroughly evaluated through both experimental and simulation approaches. In-situ UV irradiation yielded a 4-fold increase in SERS intensity, enabling a thiram detection limit of 10^{-9} M. The prepared substrates demonstrated exceptional reusability and durability, maintaining high performance over extended periods. The combination of experimental data with simulations provides a comprehensive understanding of the PIERS effect, highlighting the method's potential for highly sensitive, reliable, and versatile analytical applications.

1. Introduction

The initial observations of phenomena related to Surface Enhanced Raman Scattering (SERS) were documented by Fleischmann et al. in 1974 [1]. Van Duyne et al. later elucidated the optical phenomenon of amplified Raman signal intensities from roughened silver electrodes, formally designating it as SERS [2]. Subsequently, theoretical frameworks were developed to provide a mechanistic understanding of this effect.

The SERS framework encompasses an electromagnetic (EM) amplification mechanism originated from localized surface plasmon resonance (LSPR) excitation caused by the collective oscillation of electrons in metal nanoparticles [3,4]. Conversely, a chemical mechanism (CM) associated with SERS involves the charge transfer (CT) process between the substrate and the analyte [5,6]. However, it has been validated that EM is the predominant mechanism that contributes to SERS, with an enhancement factor of approximately $10^6 - 10^{10}$ [7,8]. Since then, many

studies have aimed to improve SERS substrates with a variety of structures, compositions, sizes, shapes, environments, and interactions with different analytes [9–11]. Improvements are often aimed at generating “hot spots” associated with LSPR coupling in nanogaps between noble metal nanostructures [12]. However, material optimization seems to encounter a temporary enhancement threshold.

Despite the fact that CM exhibits a notably lower enhancement factor, it tends to attract certain attention because it helps to understand the molecular interaction and charge transfer process between molecules and metal surfaces [13]. But if the enhancement factor is increased, even by just an order of magnitude, the sensitivity will be significantly improved, which is really meaningful in practical applications. Recent studies introduce a new concept of controlling chemical enhancement via external excitation using an appropriate light source, namely photo induced surface enhanced Raman scattering (PIERS) [14].

The PIERS effect enables an additional chemical enhancement of the Raman signal induced by the interaction of irradiation with

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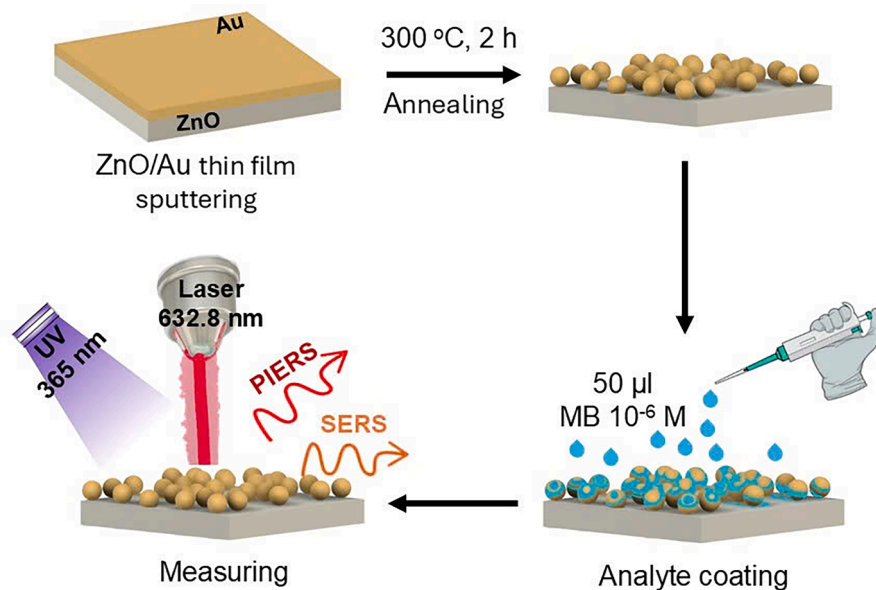


Fig. 1. Schematic diagram of sample fabrication, SERS, and PIERS analysis.

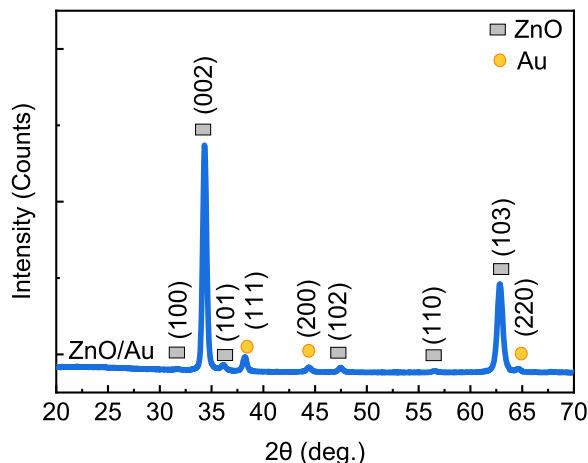


Fig. 2. X-ray diffraction pattern of ZnO@Au thin film.

semiconducting substrate. A recent study by Parkin et al. reported that the TiO₂/(Au and Ag) SERS substrate provides Raman signal with significant amplification when pretreated with ultraviolet (UV) light for a period of time [15]. This phenomenon is called photo induced enhanced

Raman spectroscopy (PIERS). Later study shows that there are several modifications of photo excitation process [16,17]. First, SERS substrates could be irradiated with appropriate light for a period of time, and then Raman probe was deposited onto the prepared SERS substrate. This may be referred to as substrate irradiation [18,19]. Second, SERS substrate is deposited with an analyte and then subjected to light irradiation for a period of time prior to Raman measurement, which can be named as sample irradiation [20,21]. Lastly, some recent studies demonstrate that PIERS can also be achieved by simultaneous irradiation of an additional light source other than the that for Raman excitation [4,22].

While most of the reported studies focused on the first and second approaches, where it is believed that generation of oxygen vacancies is the main reason for Raman enhancement. To generate enough oxygen vacancies the sample pre-irradiation process often takes a long time, which unintentionally disadvantages the rapidity of Raman measurements. In addition, the method of irradiation of the substrate and analyte can sometimes cause bleaching, affecting the accuracy of the measurement or sample degradation. Meanwhile, the method of simultaneous photo excitation has shown many advantages, such as time saving and ability to be performed on-site but remains underexplored. Raman measurements under simultaneous UV illumination allows to control the enhancement process as it occurs at the same spot. This approach is simple, fast and conveniently accessible via experiment. Furthermore, the reusability and long-term stability of PIERS substrates

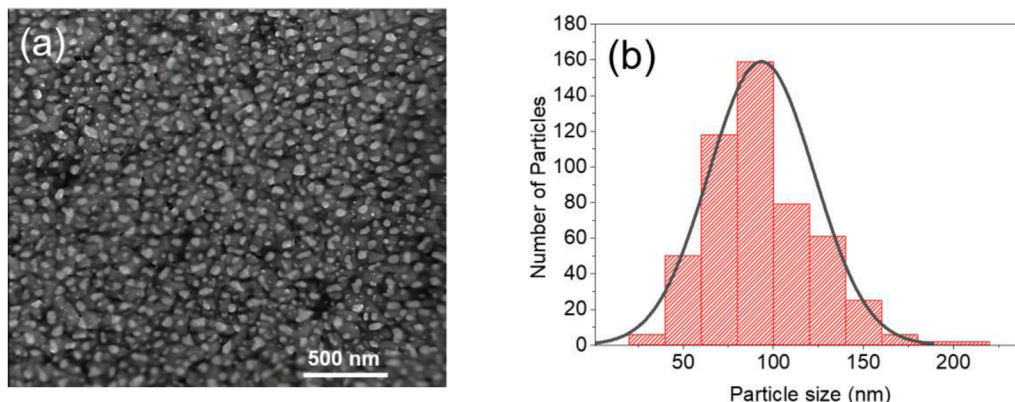


Fig. 3. (a) SEM image of a ZnO@Au thin film and (b) the corresponding size distribution of Au nanoparticles.

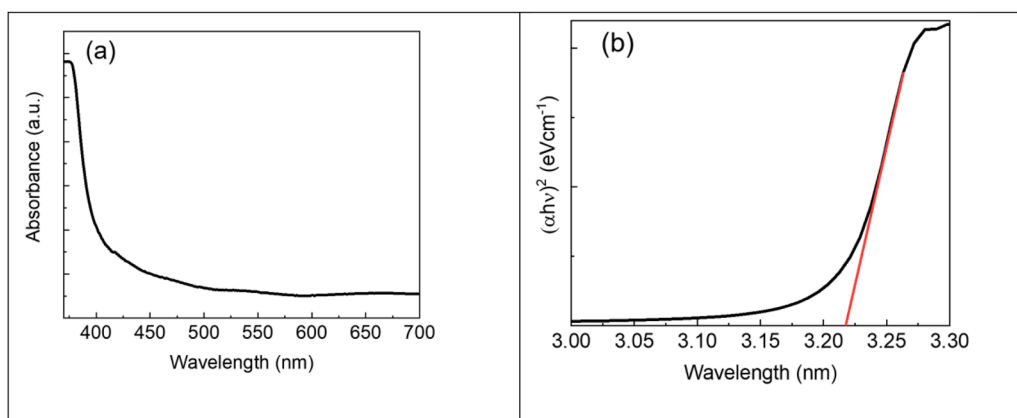


Fig. 4. (a) Absorption spectrum of the ZnO thin film; (b) Tauc plot of the ZnO thin film.

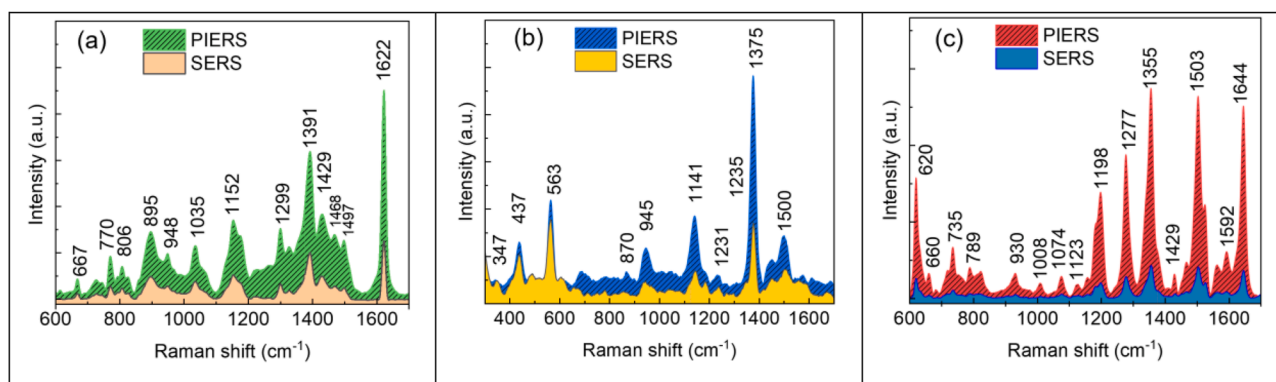


Fig. 5. PIERS and SERS spectra of different analytes 10^{-6} M: (a) Methylene blue, (b) Thiram and (c) R6G measured on ZnO@Au thin films.

have not been systematically investigated.

This research reveals the PIERS effect on ZnO@Au SERS platforms, showcasing enhanced Raman signals achieved through in situ UV irradiation. ZnO@Au thin films were fabricated via r.f. magnetron sputtering and post-annealing, providing a simple and scalable method for substrate preparation. The PIERS effect resulted in notable enhancement compared to conventional SERS, without any prolong treatment of sample or substrate prior to Raman measurement and a very low LOD of 10^{-10} M for a variety of environmental pollutants such as Methylene Blue, Thiram, and Rhodamine 6 G (R6G). Additionally, experimental results combined with simulations based on model extracted from experimental data demonstrate that the enhancement originates from photoinduced electron-hole generation in ZnO and charge transfer through semiconductor and Au junction, leading to changes in electron density in plasmonic nanostructures. The FDTD simulations in this study are not based solely on ideal spherical particle models but on realistic surface morphology data extracted from SEM images of real SERS substrates, allowing us to generate simulations that closely reflect the actual structured nano configuration. To the best of our knowledge, we believe that FDTD simulation for PIERS performed on model extract from real samples has not been published before. As a result, the simulated field distributions and enhancement regions are more representative of what occurs in the real nano system, providing a more objective and physically meaningful interpretation of the PIERS behavior on ZnO@Au thin-film SERS substrates. The combination of dynamic measurements and morphology-based simulations provides more realistic and direct insight into how the PIERS effect operates on scalable planar thin-film platforms.

Furthermore, we also demonstrate that the prepared ZnO@Au thin films can serve as PIERS platform with excellent reusability. These

findings provide valuable insights for the development of next-generation integrated SERS substrates and highlight the potential of in situ PIERS for high-sensitivity environmental monitoring and pesticide residue analysis at ultra-low concentrations. The prepared ZnO@Au thin film SERS substrates demonstrate potential applicability in transmission-mode SERS configurations, where light needs to pass through the substrate. This is highly relevant in emerging areas such as microfluidic devices, lab-on-a-chip platforms, or even non-destructive analysis in cultural heritage, where transparent or semi-transparent SERS substrates are desirable.

2. Experimental

Glass slices with dimensions of $20 \times 20 \times 1$ mm were subjected to a sequential ultrasonic cleaning process using acetone, ethanol, and deionized water, followed by nitrogen gas drying. Next, ZnO thin films were subsequently fabricated onto these substrates by RF sputtering using a Mini ULVAC system (Japan). The vacuum chamber was initially pumped down to 3×10^{-6} Pa before introducing argon gas to stabilize the working pressure at 1 Pa. The sputtering of the ZnO thin films was carried out at a power of 175 W for 20 min without substrate heating. The thickness of the ZnO coating was measured using a surface thickness gauge system, Veeco Dektak 150 – USA (see Supporting Information). The results showed that the ZnO thin film had a thickness of about 600 nm (Fig. S1). In the next step, an Au layer was deposited on the previously synthesized ZnO thin films and on glass substrates (as control samples) using DC sputtering (JEOL JFC - 1200). The gold deposition was conducted at 20 mA for 40 s. The prepared ZnO/Au thin films were annealed at 300 °C for 2 h under ambient conditions to obtain ZnO thin film decorated with Au nanoparticles (ZnO@Au). The diagram of

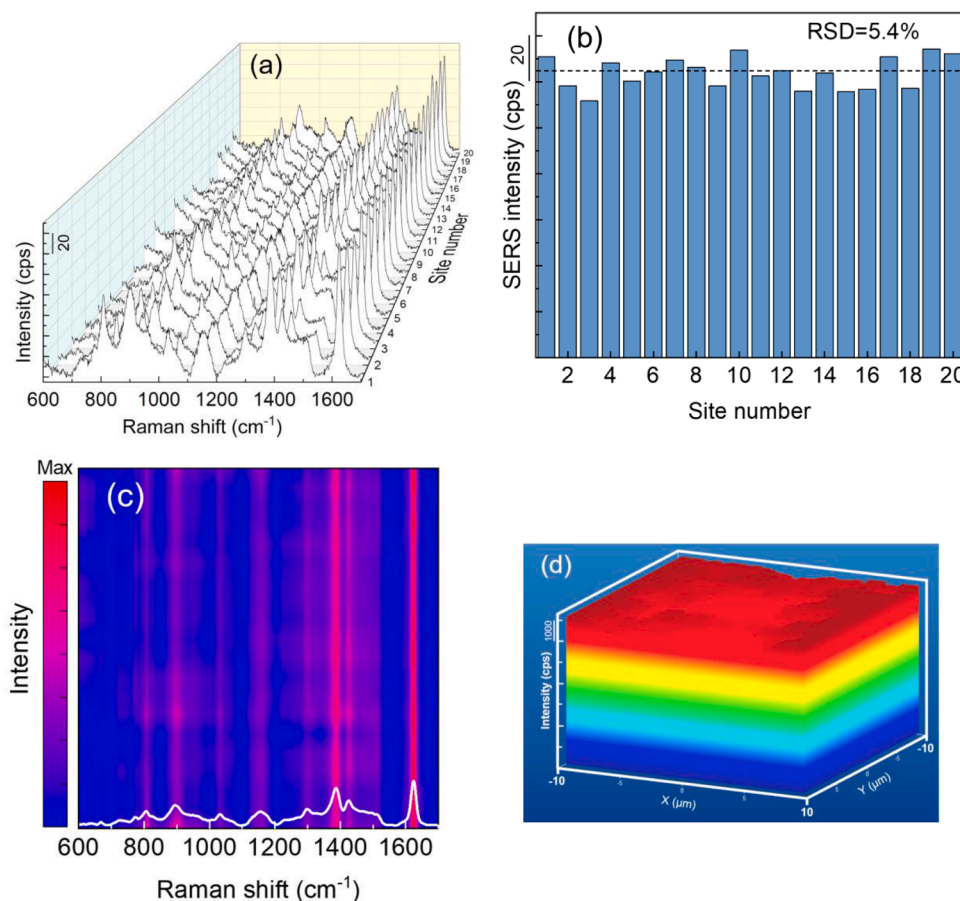


Fig. 6. (a) SERS spectrum of the ZnO@Au thin film measured at 20 random points over an area of $20 \times 20 \mu\text{m}^2$; (b) Column chart showing variation of intensity of 1622 cm^{-1} peak; (c) 2D intensity map of SERS spectra from 20 sites across the ZnO@Au thin film; (d) 3D Raman intensity map at 1622 cm^{-1} over a $20 \times 20 \mu\text{m}^2$ area of the ZnO@Au thin film substrate.

sample preparation is shown in Fig. 1. Finally, the samples were allowed to cool down naturally under ambient conditions. Methylene blue (MB), Thiram, and Rhodamine 6 G (R6G) solutions were used as Raman probe in this study. Fixed volumes of $50 \mu\text{l}$ MB of different concentrations were dropped onto the investigated samples. The samples were dried naturally before Raman spectra acquisition. The influence of UV light on Raman signal enhancement was studied using a UV LED (365 nm , 1 mW , 10 nm bandwidth) directed at a 45° angle relative to the sample surface. The distance between the LED and sample was fixed at 10 cm (Fig. 1), and Raman spectra were recorded both with and without UV illumination at the same measurement point for comparison.

Characterization techniques included X-ray diffraction (XRD) using a PANalytical Empyrean diffractometer ($\text{Cu K}\alpha$ radiation, $\lambda = 1.54056 \text{ \AA}$) to examine crystal structure, and scanning electron microscopy (JEOL JSM – IT100) for surface morphology analysis. Absorption spectra were measured using a Shimadzu UV – 2450 spectrophotometer. Raman spectroscopy was performed using a Horiba Jobin Yvon LabRAM HR 800 system equipped with a 632.8 nm He-Ne laser as excitation source. To evaluate the structural and optical properties, measurements such as XRD, SEM, EDS, and UV–Vis were conducted multiple times on independently prepared samples to ensure reproducibility and consistency. For SERS and PIERS measurements, spectra were collected at different points on each substrate and repeated over multiple experimental runs, including reuse of the same substrate after UV irradiation, to assess the uniformity and stability of the signal enhancement.

3. Results and discussion

The crystal structure of the ZnO thin film were studied by X-ray diffraction (Fig. 2). The results show that all characteristic peaks of the obtained thin film are consistent with JCPDS No. 36–1451 of the hexagonal wurtzite structure of ZnO [23]. The dominated peak at position $2\theta = 34.31^\circ$ in the pattern also implies a preferential orientation of (002) plane. The calculated lattice constants are $a = 3.258 \text{ \AA}$, and $c = 5.225 \text{ \AA}$, which are very close to previously published values [24,25]. In addition, the crystal size, estimated from Debye Scherrer equation, is $D = 24 \text{ nm}$ [26]:

$$D = \frac{0.89\lambda}{\beta \cos \theta}$$

where D is the crystal size, λ is the wavelength of the $\text{Cu K}\alpha$ source, θ is the Bragg diffraction angle, β is the width at half maximum (FWHM) of the peak. The clear Au peaks confirm the existence of the sputtered Au layer structures.

SEM images of the ZnO@Au thin film annealed at 300°C for 2 h are shown in Fig. 3. As can be seen in the SEM image, the Au layer was transformed into nanoparticles evenly distributed on the ZnO thin film. Au nanoparticle size distribution was calculated using statistic of size data of about 500 particles. The average size was estimated to be 93 nm (Fig. 3b). The EDS spectrum in Fig. S2 shows that the ZnO@Au thin film is composed of only Zn, O, and Au elements. This implies high purity of the ZnO@Au thin film.

Fig. 4a displays the UV–vis absorption spectrum of the ZnO thin film,

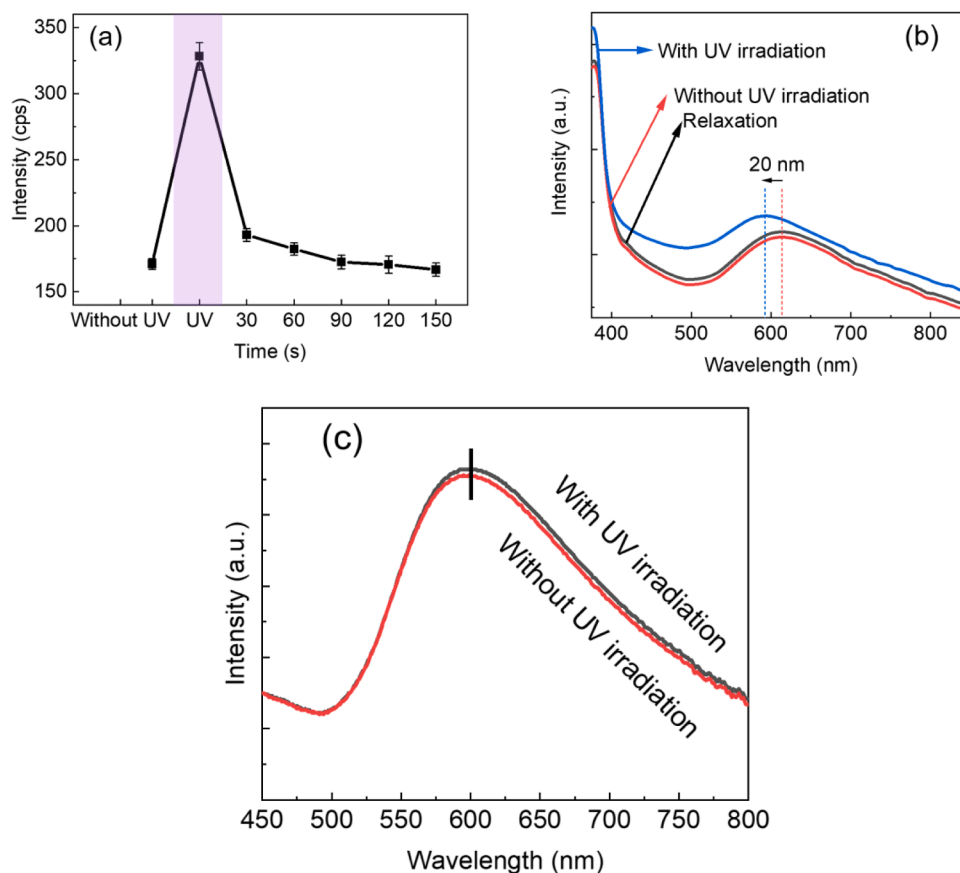


Fig. 7. (a) Variation of Raman intensity at 1622cm^{-1} before, under, and after UV excitation; (b) Absorption spectrum of ZnO@Au thin film before, during, and after UV irradiation; (c) Absorption spectrum of Au thin film before and during UV irradiation.

revealing an absorption edge near 375 nm. The band gap (E_g) of ZnO thin film is determined using the Tauc relation for the allowed direct transition [27]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$

where α is the theoretical absorption coefficient, $h\nu$ is the photon energy, E_g is the direct band gap, and A is a constant. Fig. 4b shows the Tauc plot with extrapolation of the linear part intersecting the energy axis. The band gap energy estimated for the ZnO thin film is 3.22 eV.

Fig. 5a shows the SERS spectrum of Methylene blue at a concentration of 10^{-6} M. It can be seen that the characteristic peaks of Methylene blue are clearly shown at peaks 1622, 1497, 1468, 1429, 1391, 1299, 1152, 1035, 948, 895, 806, 770, and 667 cm^{-1} [28,29]. Similarly, the clear SERS spectrum of 10^{-6} M Thiram was observed, the enhancement with main peaks at positions 1500, 1357, 1231, 1141, 945, 870, 563, and 437 cm^{-1} (Fig. 5b). All the peaks of Thiram are consistent previous publications [30–32]. The Raman enhancement was also observed for R6G reagent as shown in Fig. 5c. The results demonstrate that the ZnO@Au thin film serves as a good SERS substrate.

It should be noted that under in situ UV excitation, SERS signal intensity was significantly improved. The photo induced enhancement factors (EFs), defined as the Raman intensity under UV excitation divided by intensity without UV, are 4.1, 2.8, and 6.3 for MB (at 1622 cm^{-1}), Thiram (at 1375 cm^{-1}), and R6G (at 1355 cm^{-1}), respectively. The high enhancement factors indicate that the sensitivity and resolution of the Raman measurement was significantly improved, allowing for a more detailed analysis of the structure and properties of the substances in the sample.

In PIERS, the wavelength of excitation source plays a critical role. Fig. S3 shows the Raman spectrum of Methylene blue on a thin film of

ZnO@Au before and after excitation by a light source with wavelength of 400 nm. It can be clearly seen that the intensity of the MB vibration modes are almost identical to that of the spectrum collected without additional excitation. This result can be explained when considering the energy of the excitation photon and the bandgap of ZnO. The energy of a UV lamp with a wavelength of 400 nm ($\sim 3.1\text{ eV}$) is lower than the band gap energy of ZnO ($\sim 3.22\text{ eV}$). When UV light with wavelength of 365 nm (3.39 eV) is applied, the photons with energy higher than the band gap of ZnO facilitate the generation of electron-hole pairs efficiently. Then the electrons will be transferred to Au nanoparticles via ZnO@Au junction.

The uniform enhancement, governed by the distribution of the plasmonic nanostructures, is an indicator for the quality of the prepared SERS substrate. In this study, we conducted a survey of 20 random measurement points over a $20 \times 20\text{ mm}$ area on a ZnO@Au thin film. The statistical map of the obtained SERS spectrum is shown in Fig. 6a. The average SERS intensity of the 1622 cm^{-1} characteristic peak and the relative standard deviation (%RSD) were evaluated to study the point-to-point uniformity. The results showed that the calculated relative standard deviation RSD was only 5.4 % (Fig. 6b). The obtained results demonstrate that the ZnO@Au thin film substrate serves as a highly uniform SERS substrate, which is extremely important for quantitative chemical analysis applications. In addition, a 2D intensity map was constructed to visualize the overall spectral uniformity across the measured area (Fig. 6c). Furthermore, we performed detailed analysis on a $20 \times 20\text{ }\mu\text{m}^2$ area on the ZnO@Au thin film to further confirm the uniformity of the enhancement. A 3D Raman intensity map was constructed from the same dataset (Fig. 6d), providing a clear and intuitive image of the signal distribution. This result shows that the ZnO@Au thin film SERS substrate exhibits relatively uniform enhancement performance over the entire scanning area, indicating its reliability for

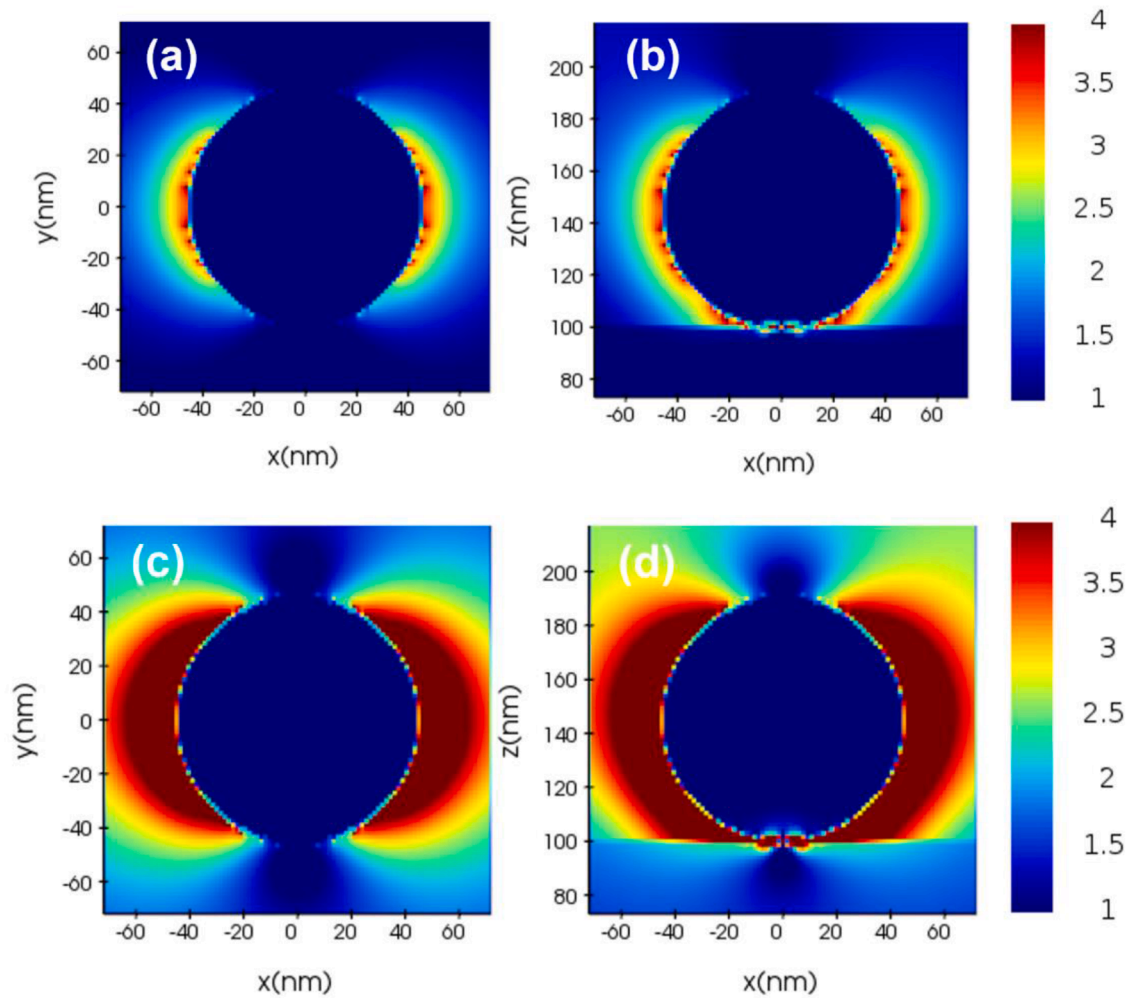


Fig. 8. Spatial distribution of the electric field of a 90 nm diameter Au nanoparticle structure on a ZnO thin film excited by a 632.8 nm source: (a) XY plane, (b) XZ plane. Spatial distribution of the electric field of a 90 nm diameter Au nanoparticle structure on a ZnO thin film excited simultaneously by 632.8 and 365 nm sources: (c) XY plane, (d) XZ plane.

practical SERS sensing applications.

Research on the mechanism of the PIERS effect is really important to clarify the contributing factors so that optimization can be proposed. In previous studies on PIERS where sample or substrates were shone with UV irradiation, the general mechanism proposed is the formation of oxygen vacancies in semiconductors [33]. In addition, the experiments showed that after stopping the UV excitation, there was a gradual relaxation of PIERS signal to the original level. The relaxing effect can take place within a few minutes to several tens of minutes, depending on the irradiation conditions as a result of the healing process of oxygen vacancies. Therefore, the relaxation time can be used to partially clarify the mechanism of the PIERS effect. In our study, the relaxation effect was investigated by monitoring Raman intensity before, under and right after UV excitation. As can be seen in Fig. 7a, under UV stimulation, the intensity of the Raman signal is clearly enhanced compared with the original spectrum. After stopping UV excitation, the PIERS signal quickly relaxed to the original level.

The experimental data suggested that formation of oxygen vacancies can be excluded. We believe that the enhancement of Raman intensity in our case comes from electron-hole pairs generation under in situ UV irradiation during Raman measurements. To further confirm this assumption, absorption measurements were performed on ZnO@Au thin films and Au thin films with the same fabrication conditions. Absorption spectra of ZnO@Au thin films without and with UV stimulation were collected to clarify its contribution. Fig. 7b clearly shows the blue shift of

the 600 nm wide peak region, which can be assigned to the plasmon resonance of Au nanoparticles upon UV irradiation. This plasmon peak shifts back to 610 nm after removing the UV irradiation. This blue shift can be explained by the increase electron density in Au nanoparticle due to charge transfer from the ZnO semiconductor. According to Mulvaney, it is possible to estimate the relative change in electron density using the equation [34]:

$$\frac{\Delta N}{N} = -\frac{2\Delta\lambda}{\lambda_0}$$

where $\Delta\lambda$ is the wavelength shift (~ 20 nm), and λ_0 is the maximum position of the plasmon peak of Au nanoparticles. The electron density transferred to Au was estimated to be 6.5 %. It should also be noted that the peak shift was not observed for the Au thin film under the same conditions. The result indicates the important role of ZnO in the charge generation and transfer process as well as in enhancement of Raman signal under excitation (Fig. 7c).

Typically, the enhancement of the SERS substrate is closely dependent on the enhancement of the local electric field (EM) intensity of the nanostructure. In this study, to better understand the influence of the “hot spot” distribution of the Au nanostructure on the ZnO thin film, as well as the impact of UV excitation on EM and absorption changes of the plasmon resonance peak region of the Au nanostructure, we used the Finite-Difference Time-Domain (FDTD) method to simulate the local electric field spatial distribution. The data of the real and imaginary

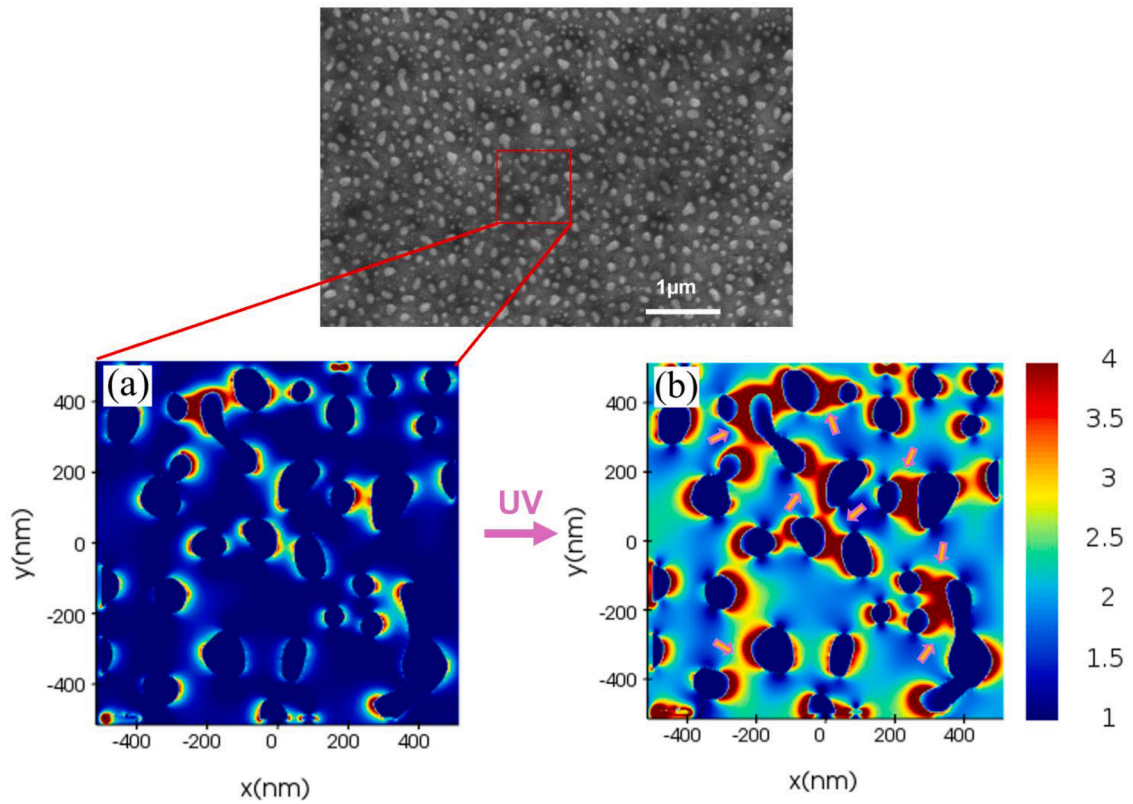


Fig. 9. Spatial distribution of the electric field in the XY plane of the ZnO@Au structure modeled from SEM images excited by: a) 632.8 nm irradiation, (b) 632.8 and 365 nm irradiation simultaneously.

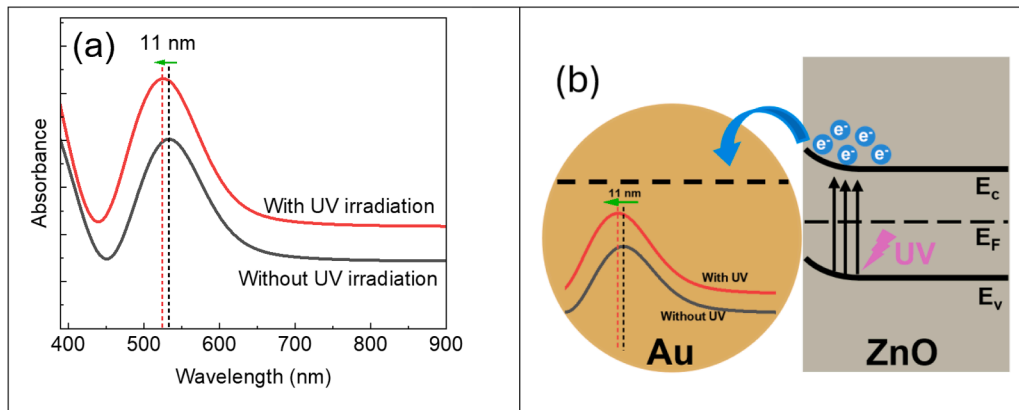


Fig. 10. (a) Simulation of UV-Vis absorption of ZnO/Au structure before and after UV excitation, (b) schematic illustration of the PIERS mechanism on ZnO/Au thin film under UV irradiation.

parts of the dielectric constant of Au in the simulation were extracted from the experiments of Johnson and Christy [35], while the ZnO data were obtained from the studies of Lorenzo Fanni, et al. [36]. The refractive index of the surrounding air medium was set to $n = 1$ and the temperature was set to 300 K. The simulation model includes a spherical Au nanoparticle with a diameter of 90 nm on a 200 nm thick ZnO thin film. The simulation data are shown in Fig. 8. Then, to study the interaction between Au nanostructures on ZnO thin films as close to reality, we introduced a ZnO@Au structure model based on SEM images with dimensions of $1 \times 1 \mu\text{m}$.

The structures (including Au nanoparticles and ZnO substrate) were placed in a mesh volume with perfectly matched layer boundaries (PML) to avoid wave reflections from the system edges and a fine cubic mesh divided by 1 nm step. For excitation, two total scattered field (TFSF)

sources were used: a source representing a 632.8 nm excitation laser corresponding to a 4.2 fs sinusoidal pulse placed perpendicularly above the structures and a 365 nm UV excitation source. The absorption spectrum of the ZnO@Au thin films was simulated in the range of 200 – 900 nm.

The EM simulation calculations were performed in two stages. First, the electric field intensity and absorption were calculated with only 632.8 nm excitation. Then, 365 nm UV excitation was added to clarify the contribution of UV excitation. The output data represents the electric field intensity distribution normalized with respect to the incident field $\left(\frac{E}{E_0}\right)^4$. A comparison of the simulated electric field distributions for the ZnO@Au thin film is shown in Fig. 8. Compared with the excitation of

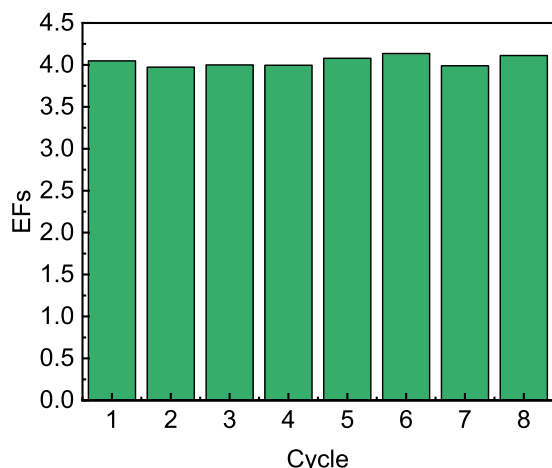


Fig. 11. PIERS enhancement factor on ZnO@Au thin film after 8 cleaning cycles.

632.8 nm light only (Fig. 8a-b, a stronger EM near-field enhancement can be clearly observed with the addition of UV excitation (Fig. 8c-d).

The actual morphology of the Au nanostructures was extracted from SEM images using a grayscale thresholding method to approximate particle boundaries. The resulting geometry was converted into a binary mesh and imported into the simulation environment to preserve the inter-particle gaps and overall surface topography observed in the experimental sample. The simulation domain was $1 \times 1 \mu\text{m}^2$. The surrounding medium was set as air ($n = 1$), and optical constants of Au and ZnO were taken from Johnson & Christy and Lorenzo Fanni, et al. [37]. A fine mesh of 1 nm and perfectly matched layer (PML) boundaries were used. Two excitation sources were applied: a 632.8 nm laser and an additional 365 nm UV source. The 632.8 nm excitation was polarized in-plane and propagated perpendicular to the surface (Z axis). Fig. 9a shows the electric field distribution under 632.8 nm excitation alone, while Fig. 9b illustrates the enhanced field under simultaneous 365 nm UV and 632.8 nm illumination. The SEM-based model shows that the gap regions of the nanoparticles and the adjacent Au nano-islands have strong electric field intensities due to the strong localized surface plasmon resonance (Fig. 9b). The simulation results support the experimental results, demonstrating a significant electric field enhancement after UV excitation. The absorption spectrum of the ZnO@Au thin film showed a blue-shifted peak upon simultaneous UV excitation, consistent with the experimental data. Cross-sectional absorption calculations also showed a significant blue-shift of the Au plasmon resonance peak (Fig. 10a), consistent with the experimental results (Fig. 7b).

The mechanism of the PIERS effect is illustrated in Fig. 10b. When irradiated with UV light in situ, ZnO absorbs UV photons and generates electron-hole pairs. The photogenerated electrons are transferred from the conduction band of ZnO to the Au nanoparticles through the

Schottky barrier. This interfacial charge transfer increases the electron density in Au, resulting in a shift of the localized surface plasmon resonance (LSPR) peak toward shorter wavelengths (blue shift). The increased electron density in the Au nanostructures not only changes the plasmonic behavior of Au but also enhances the local electric field at the Au nanoparticle surfaces. These enhanced plasmonic “hot spots” are important for amplifying the Raman signals of the probe molecules adsorbed on the surface.

To the best of our knowledge, the reusability of PIERS substrates utilizing ZnO@Au materials has not been extensively studied. Reusability is crucial, as it not only reduces analysis costs but also facilitates quantitative assessments of Raman scattering cross sections for various analytes. In this study, we explored the recyclability of ZnO@Au-based PIERS substrates by leveraging the photocatalytic properties of ZnO@Au thin films. After Raman spectral acquisition, the ZnO@Au SERS substrates were subjected to 365 nm UV irradiation for 5 h to photocatalytically decompose any residual analytes, as depicted in Fig. S4. To minimize potential contributions from residual oxygen vacancies possibly induced during UV treatment, the cleaned ZnO@Au thin films were allowed to rest in dark for 8 h. Subsequently, the SERS substrates were re-functionalized with 10^{-6} M methylene blue (MB) to evaluate the PIERS effect of the UV-cleaned substrates. Fig. 11 presents a bar graph of the enhancement factors (EFs) at the 1622 cm^{-1} vibrational mode after 8 cleaning cycles. The minimal fluctuations in EFs demonstrate the good reproducibility of the ZnO@Au SERS substrates, confirming the reliability of the Raman signal across multiple cycles.

The durability of the ZnO@Au thin film SERS substrate is crucial for the PIERS effect, as prolonged UV exposure can induce material degradation, leading to diminished Raman enhancement. The durability of the ZnO@Au structure can be compromised by several factors, including oxidation, surface structure modifications. Environmental conditions like pH, temperature, and chemical exposure can also degrade the SERS effect by affecting the structure’s durability. To ensure stable and robust SERS signals, preserving the ZnO@Au structure’s integrity is paramount. In this study, we investigated the long-term stability of ZnO@Au thin films stored under ambient conditions at room temperature for one year. Fig. S5 presents the PIERS spectra of MB measured on both freshly prepared and one year old samples. The clear visibility of MB’s characteristic peaks in the aged sample demonstrates the high durability of the ZnO@Au SERS substrates.

Fig. 12a and Fig. 12b show the SERS spectra of MB with concentrations ranging from 10^{-7} down to 10^{-10} M and R6G with concentrations ranging from 10^{-6} down to 10^{-10} M, respectively. The detection limit for MB and R6G on the ZnO@Au thin-film SERS substrate is approximately 10^{-9} M for both MB and R6G as the characteristic peaks of the analytes become barely observable at a concentration of 10^{-10} M. However, during in-situ UV treatment, the peaks at 1622 cm^{-1} and 1391 cm^{-1} for MB and the peaks at 1646 ; 1503 ; 1356 ; 1277 and 620 cm^{-1} for R6G are readily observable. The development of PIERS for analytical uses significantly lowers detection limits, making it a valuable technique for

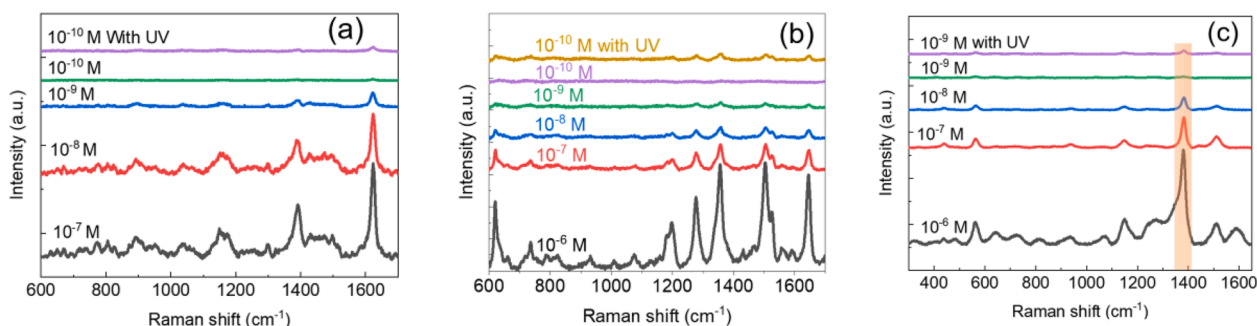


Fig. 12. Raman spectra of (a) MB, (b) R6G, and (c) Thiram measured on ZnO@Au substrates at different concentrations without UV excitation, together with spectra recorded under UV excitation.

detection of analytes at lower concentrations than those used in conventional SERS measurements.

Thiram, a widely used fungicide in agriculture, has raised significant concerns due to its potential toxicity [37,38]. Taking into account the risks associated with exposure to thiram even at very low concentrations, particularly its impact on human health and the environment, the European Union has banned the use of thiram on certain agricultural products [39]. It is important to develop more sensitive methods for its detection at very low concentrations. The practical applicability of PIERS platforms based on ZnO@Au thin films was demonstrated by capability of trace detection of thiram. The results demonstrated that limit of detection by PIERS technique is 10^{-9} M (Fig. 12c). This represents a significant improvement in the sensitivity of the detection method, allowing the determination of thiram at concentrations well below the threshold of conventional SERS (10^{-8} M). Such low detection limits are extremely important for application in the field of food safety or environmental monitoring, where monitoring toxic substances at trace level is recommended.

4. Conclusions

In this work, we developed an efficient ZnO@Au thin film SERS substrate using radio frequency magnetron sputtering and post-annealing techniques. The substrate's high homogeneity contributed to its outstanding performance. The study also shows that SERS, assisted with UV excitation, enabled a fourfold enhancement of the SERS signal intensity and notably lower the detection limit of Methylene blue and Thiram by one order of magnitude. The ZnO@Au SERS substrates exhibited impressive reusability, maintaining high performance over 8 cycles and long-term durability. Combining experimental data with simulations provided a comprehensive understanding of the PIERS effect, suggesting that charge carrier generation and transfer play an important role in PIERS enhancement in ZnO@Au thin films. This stable, highly sensitive, and homogeneous SERS substrate offers significant advances in chemical analysis and enhanced analytical accuracy in a wide variety of applications.

CRediT authorship contribution statement

Van Tan Tran: Writing – original draft, Investigation, Data curation. **Nguyen Hai Pham:** Writing – review & editing, Investigation. **Viet Tuyen Nguyen:** Writing – review & editing, Validation, Methodology, Investigation, Data curation, Conceptualization. **The Kien Pham:** Investigation. **Canh Viet Nguyen:** Project administration, Investigation. **Thi Ngoc Anh Tran:** Investigation. **Cong Doanh Sai:** Investigation. **Cong Toan Nguyen:** Investigation. **Quang Hoa Nguyen:** Investigation. **Trong Tam Nguyen:** Investigation. **Thi Hong Pham:** Investigation. **Thi Hai Yen Le:** Investigation. **Minh Phuong Le:** Investigation. **Thanh Long Nguyen:** Investigation. **An Bang Ngac:** Writing – review & editing, Investigation, Funding acquisition. **Thi Ha Tran:** Writing – review & editing, Supervision, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.surf.2025.107738.

Data availability

Data will be made available on request.

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