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Flexible SERS substrates for hazardous materials detection: recent advances

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This article reviews the most recent advances in the development of flexible substrates used as surface-enhanced Raman scattering (SERS) platforms for detecting several hazardous materials (e.g., explosives, pesticides, drugs, and dyes). Different flexible platforms such as papers/filter papers, fabrics, polymer nanofibers, and cellulose fibers have been investigated over the last few years and their SERS efficacies have been evaluated. We start with an introduction of the importance of hazardous materials trace detection followed by a summary of different SERS methodologies with particular attention on flexible substrates and their advantages over the nanostructures and nanoparticle-based solid/hybrid substrates. The potential of flexible SERS substrates, in conjunction with a simple portable Raman spectrometer, is the power to enable practical/on-field/point of interest applications primarily because of their low-cost and easy sampling.

Keywords: hazardous materials; flexible; surface-enhanced Raman scattering (SERS); nanomaterials; nanostructures

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Introduction

In the present-day scenario, human health, and environmental safety are the foremost concerns worldwide. Hazardous materials are referred to as those which have been determined to be capable of presenting an unreasonable risk to human health, safety, and property. The main characteristics of these materials are ignitability, corrosivity, reactivity, or toxicity. The specific categories among these materials are explosives, flammable liquids, gases, oxidizers, corrosives, flammable solids, radioactive materials, poisonous/infectious substances, and dangerous substances. We start with a short overview of various hazardous materials followed by the introduction of Raman spectroscopy and surface enhanced Rama spectroscopy/scattering (SERS) techniques. This review aims to report on the detection of hazardous materials such as explosives, pesticides, and simulants of chemical warfare agents using flexible SERS substrates.

Hazardous materials

Explosives/high energy materials (HEMs) are those materials that contain nitro groups (which are energetic) and release an enormous amount of energy in the form of light and heat when they are subjected to an external stimulus such as (a) spark (b) shock or even (c) friction. Explosives are commonly categorized as primary and secondary depending on their detonation (velocity, pressure etc.) and sensitivity parameters. Primary explosives are extremely sensitive and release enormous energy even with a small perturbation such as shock/collision. Therefore, the difficulty is generally high while handling the primary explosives. They act as boosters or initiators for detonating secondary explosives. Lead azide and mercury fulminate are a few examples of primary explosives, while 1,3,5,7-Tetranitro-1,3,5,7- tetrazocane (HMX), 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX), trinitrotoluene (TNT), etc. are representative of

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secondary explosives secondary explosives secondary explosives seconda. Interestingly, there are few home-prepared explosives utilized in the preparation of improvised explosive devices (IEDs). These are now easily synthesized at the laboratory level from simple molecules such as ammonium nitrate (AN), dinitrotoluene (DNT), picric acid (PA), etc.. Pesticides are the chemicals used by farmers/transporters to protect the crops/vegetables/ fruits from insects/pests/rodents. The overused pesticides will remain as residues in the food, which may cause risk to human health (cancer/allergies/intoxications) and the ecosystem (surface water/soil)[2]. Malathion, Carbofuran, methyl parathion, Carbaryl, etc., are a few examples of various pesticides available in the market. For example, thiram is the most used pesticide, which averts fungal diseases, but it causes damage to the skin and is very harmful to the health. Chemical warfare agents (CWAs)[3,4] are the chemical weapons used in a terrorist attacks, which are an intensified threat to the environment and civilian population. The principal compounds are mustard, lewisite, G-series nerve agents [Tabun (GA); Sarin (GB); Soman (GD)], and V-series nerve agents [O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate (VX)]. Sarin was used as a chemical weapon by terrorists in the 1995 exposure incident in the Tokyo subway system wherein more than 1000 people were affected. At room temperature, these are volatile liquids that cause a serious risk (paralysis, loss of consciousness, depression of the central respiratory drive) from exposure (dermal contact with a liquid nerve agent). Inhalation of the low vapor nerve agent even for a few minutes (for e.g., ~10 min) causes the contraction of the pupils of the eye, tightness of the chest, headache, rhinorrhea, etc[3]. These are extremely toxic, and their usage is restricted in non-surety laboratories because of the risk in exposure assessments. Chemical warfare agent simulants are recently developed, and they mimic the actual CWAs carrying all the relevant chemical and physical properties without accompanying their toxicological properties. Vinod Kumar et al[5]. reported the development of CWAs, their toxicity, and first usage as weapons worldwide. He discussed the different principles and chemical sensing methods of CWAs and developments in chromo-fluorogenic sensing techniques. Most of the CWA simulants are odorless, colorless, and tasteless. Distilled mustard (HD- $C_4H_8Cl_2S$), methyl salicylate (MS- $C_8H_8O_3$), 2-Chloroethyl methyl sulphide (CEMS- C_3H_7ClS), etc. are the surrogate simulants of mustard CWA. Dimethyl methylphosphonate (DMMP), di-ethyl methylphosphonate (DEMP), di-ethyl ethylphosphonate (DEEP), Diisopropyl methylphosphonate (DIMP), etc. are the simulants of G-Agent. [G-Agent named because these are first secretly synthesized by the German Ministry of Defense before and during World War II-1936] Amiton (VG), S-diethyl phenylphosphonothioate (DEPP), Malathion, parathion, etc. are simulants of VX agent.

Therefore, rapid and reliable detection of these hazardous molecules is the primary concern of both governmental agencies and research community to reduce the risk to society. Razdan and co-workers[6] have recently provided a comprehensive review on the laser based standoff detection of CWA. In this review, they clearly tabulated the classification, toxicity (lethal dose), and other important properties of the CWA. The significant global research progress in the laser-based sensors such as Raman sensors and DIAL [differential absorption LIDAR (light detection and ranging)] sensors in the detection of CWA. There exists a variety of analytical methods (reported in the literature) for the detection of such hazardous materials either in residue/bulk form or in concealed places. Some of the tested and mature techniques include ion-mobility spectroscopy (IMS), terahertz (THz) spectroscopy, laser-induced breakdown spectroscopy (LIBS), Raman spectroscopy and variants, photo-acoustic, and gas chromatography, etc[7−14]. Some of these techniques either cause partial sample destruction or require isolation of sample, which is very difficult in the case of traces. Additionally, a few of these techniques do not favor the usage of low quantity samples and require a skilled person for instrument calibration and measurements. Furthermore, high water absorption, poor specificity, and difficulty in instrumentation limit the usage of these techniques for on-field explosive detection[15,16].

Raman spectroscopy and variants

Raman spectroscopy is a simple, rapid, and a non-destructive spectroscopic technique based on molecular vibrations as signatures in the spectra. The Raman spectrum of any analyte molecule provides specific information and conveys chemical/structural information. This is important in the case of explosives (in pure form or even in the mixture form) irrespective of solid, liquid, powder, or gas state[17−22]. However, Raman scattering is a very weak process and, consequently, requires either large quantities of the analyte or high input laser powers to obtain the molecular signatures. Surface-enhanced Raman scattering is one of the advanced and developed Raman techniques for overcoming these limitations (intrinsically low Raman signal intensity for low concentration of the analyte molecules)[1]. This is based on the huge electric field enhancements in the vicinity of nanostructured metals resulting in a strong Raman signal.

In the present times, flexible SERS substrates have received great interest due to them possessing the advantages of (a) easy sampling by swabbing/wrapping directly on any curved/rough surfaces (b) large scalability by printing/roll to roll manufacturing/electrospinning etc. and (c) low overall cost of the sensing system. The development of handy flexible substrates with compact Raman devices/smart-phones can possibly provide portable sensors in real-world sensing/safety applications and serve as a powerful analytical tool for on-field analysis. For example, the possibility of detection of ultralow concentrations [picomolar (10^{-12} M or pM) to femtomolar (10^{-15} M or fM)] of two nerve gases, VX and Tabun was reported recently by Hakonen et al[23]. using flexible Au covered Si nanopillars (SERS substrates) and, significantly, using a handheld Raman spectrometer. Furthermore, the time involved in a typical detection can be reduced to practically acceptable levels (<5 sec) using these portable and low-cost disposable SERS substrates.

Surface-enhanced Raman scattering (SERS)

Martin Fleischmann and co-workers had reported a fortunate discovery way back in 1974, in which they observed enhanced Raman signals of a pyridine molecule adsorbed on an electrochemically roughened silver surface[24]. They reported the enhancement in the Raman cross-section of pyridine vibrations by a factor of ~106. This enhancement of the Raman signal in the vicinity of the metal nanostructure was named "surface-enhanced Raman scattering." In the year 1977, Van Duyne[25] and Albrecht[26] groups separately explained the mechanism of enhanced Raman signals from the metal surface. In 1985, Moskovits et al[27]. reported all the primary explanations for the enhancement mechanisms such as (a) electromagnetic (EM) enhancement and (b) chemical (CM) enhancement. The long-range EM enhancement is attributed to the so-called localized surface plasmon resonance (LSPR) in the near-field metallic surface. The interaction of the incident EM field with metal NPs possessing negative real and small positive imaginary (absorption) dielectric constant induces a collective and coherent electron oscillations, called plasmons, in the vicinity of the NP or nanostructure (NS). The interaction of electromagnetic (EM) fields with the NPs affect their optical properties which are prevailed by the material's dielectric constant at the excitation wavelength and also the surrounding media. The plasmonic noble-metal materials (mainly Au and Ag) exhibits high SERS activity because of their LSPR in the visible region, and the materials such as aluminum (Al), gallium (Ga), platinum (Pt) palladium (Pd), titanium (Ti), bismuth (Bi), indium (In), rhodium (Rh), and ruthenium (Ru), etc. exhibit the plasmonic resonance in the deep ultraviolet (UV) region[28]. Several review articles presented throughout this review discussed the significance of various optical materials used in SERS studies. The short-range CM enhancement is due to the charge transfer mechanism between the analyte molecule and the substrate[29]. Noble-metal-free SERS materials, for example semiconductors (Si, GaAs and etc.) and two-dimensional (2D) layered materials[30,31] (MoS_2, graphene, HBN and etc.) exhibit the CM enhancement. Usually, Raman signals of the molecules can be enhanced by 10^4 to 10^{10} times because of the large EM enhancements supported and provided by the plasmonic nanostructures in close proximity (~1 nm). The CM enhancement is at least 2-3 orders of magnitude less than that of EM enhancement. During the last two decades, several scientists have extensively studied the effective parameters influencing the enhancement of the SERS signal[32,33]. Enhancements in the Raman signal is a result of several contributions and it is virtually difficult to separate them into distinct components. Several factors including the platform, SERS active material, analyte properties, excitation laser mainly affect the enhancement of the Raman signals and are illustrated and explained as a schematic in Fig. 1.

Reviews on different SERS studies

A variety of review reports on SERS have been published over the last decades addressing the issues concerned with fabrication techniques, applications, and their developments. For example, Fan et al[34]. reviewed the various fabrication studies of SERS substrates such as electron-beam lithography, focused ion beam (FIB) milling, and also template-based techniques. The advantage of these nanostructured substrates is the fine control over

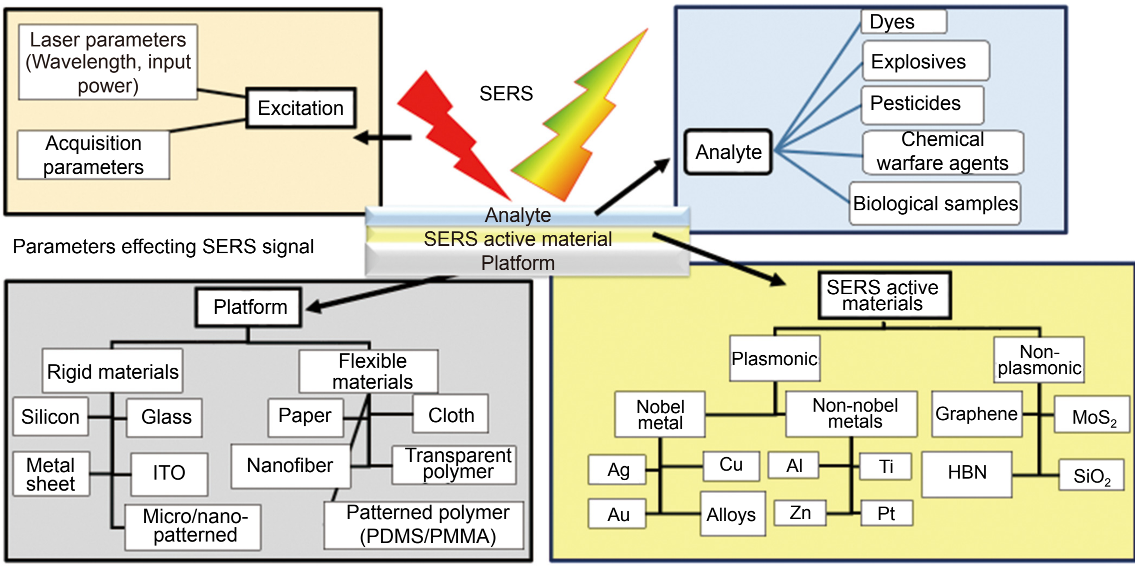

Fig. 1 | A schematic depicting the various parameters influencing the SERS signal.

the nanostructured geometries, which provide high reproducibility in the intensity of SERS signals. They discussed the application of those solid SERS substrates in biosensing, environmental, and optical fiber sensing. Mahadeva et al.[35], in the year 2015, reviewed the applications of paper as sensors in different fields like electronic devices, biosensors, strain sensors, gas sensors, and piezoelectric devices. Further, their limitations in the commercialization of these devices were also discussed. Muehlethaler et al[20]. summarized (in the year 2016) the forensic applications of SERS in the detection of explosive vapors, CWA simulant, fire accelerants, gunshot residues, etc. Mosier-Boss et al[18]. reviewed the properties of metallic SERS substrates and their usage towards the detection of various molecules such as drugs, pesticides, explosives, BTEX (benzene, toluene, ethylbenzene, xylenes), dyes, cations, and anions. Furthermore, they addressed the usage of commercially available SERS substrates. Restaino et al[36]. (2018) reviewed the point of interest sample detection using flexible and porous SERS substrates. They described the various fabrication techniques with different sample collection methods and highlighted the unprecedented ease of use of the paper sensors. Senthamizhan et al[37]. reviewed the developments of the different electrospun nanofibers (metal oxide nanofiber, composite fibers) and their use as glucose sensors in the year 2016. Hakonen et al[38]. reviewed (in the year 2015) the trends and perspectives of the SERS substrates in the detection of explosives and chemical warfare agents. Ogundare et al[39]. reviewed extensively the cellulose-based SERS platforms including their fundamentals, fabrication approaches, and application in the detection of various probe molecules. Recently, Maddipatla et al[40]. reviewed the recent approaches and the future opportunities in the development of flexible sensors in the food, environmental, and defense fields. Sun et al[19]. reviewed the on-site application of SERS by the combined portable Raman spectrometer and SERS substrates (the year 2020). The choice of an appropriate substrate is extremely essential in the SERS measurements. The requirements of an ideal SERS substrate for practical applications are a) sensitivity (able to detect very low concentrations of analyte molecules), b) uniformity (similar SERS signal strength over the entire substrate), c) reproducibility (similar data should be obtained from measurements spanning different batches, time periods etc.), d) recyclability (should be able to detect different analyte molecules with a single substrates by simple cleaning and to reduce the cost of SERS substrates), e) stability (SERS signal should not fall drastically over a period of few weeks, at least), f) flexibility (should be able to collect samples from uneven surfaces), as well as g) low fabrication cost (ideally SERS substrates should cost less since the Raman spectrometer cost is very high). A schematic of key points of SERS substrates requirements is illustrated clearly in the Fig. 2. Each of these factors and their significance are discussed in detail in the next section.

Sensitivity is the biggest virtue of a good SERS substrate is the detection of molecules at very low concentrations [traces meaning parts per billion (ppb) or parts per trillion (ppt) or parts per quadrillion (ppq)]. The

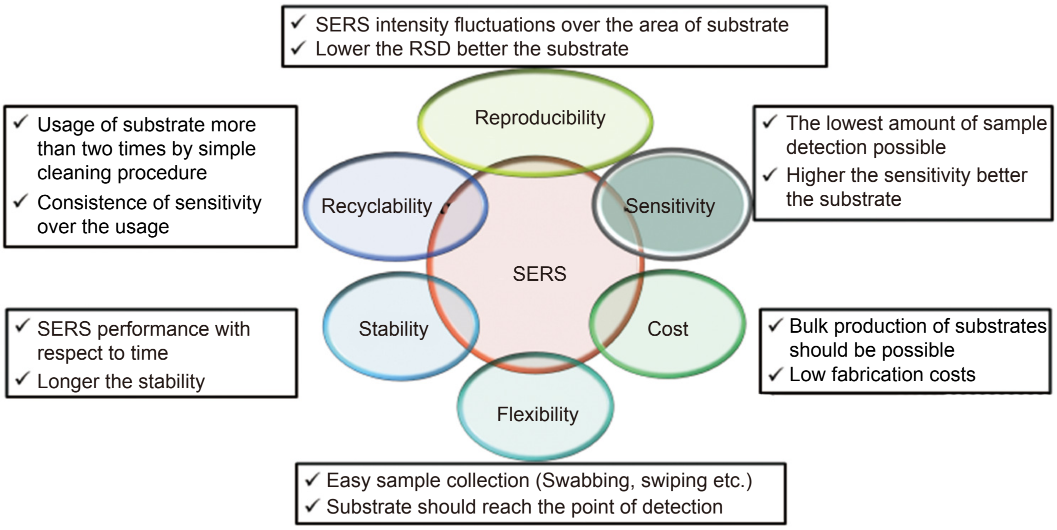

Fig. 2 | The ideal requirements of SERS substrates are summarized in this schematic.

sensitivity is generally expressed in terms of the lowest quantity of probe molecule detection possible with a given SERS substrate. The Raman signal disappears when the molecule concentrations reach a limit value. The sensitivity of the SERS substrate varies from molecule to molecule. The sensitivity of the SERS substrate is typically represented by the enhancement factor (limit of detection for a particular vibration mode of the probe molecule). Therefore, one should be judicious with the SERS substrate and select one with a higher enhancement factor or a lower limit of detection (LOD) over a wide range of analytes. Reproducibility is related to the variation of SERS intensity of the probe molecule over the NS surface. The smaller the variation in the signal, the higher the reproducibility and it is generally reported in terms of RSD (relative standard deviation) of the SERS signal. This depends mainly on the distribution of hotspots on the substrate. Low reproducibility of any SERS substrate affects the potential usage in practical applications. It is highly challenging to produce a highly reproducible SERS platform along with a homogeneous distribution of hotspots. The fluctuations of the SERS signals are calculated statistically with RSD of the particular mode intensity in the SERS spectrum. The magnitude of %RSD, indicative of the coefficient of variation, provides uncertainty in the measurement. Lower RSD values indicate a superior substrate in terms of reproducibility. Recyclability is another essential factor to test the usage of the same SERS substrate after detecting one/two molecules followed by proper cleaning procedures[41]. Xu et al[42]. developed recyclable hedgehog-shaped CuO NWs/Cu_2O hetero NSs (with Ag coating) as SERS substrates. These hetero NS have demonstrated strong SERS activity (85% retained after 7 cycles of usage) driven by a broad band visible-light photocatalytic degradation process. Ag/CuO NWs/Cu_2O composites were fabricated by ns laser ablation and subsequent thermal oxidation on the Cu sheet to develop Cu NWs on the grooved surface which was subsequently followed by Ag NPs deposition. The recyclability measurements were performed with the MG molecule by demonstrating seven-times consistent SERS performance. Stability is related to the variation of the sensitivity of SERS substrate with respect to time. This aging effect for the SERS substrates is also another important factor for storage in air/vacuum for days/months/year and their performance afterwards. Finally, the fabrication cost of the substrates is very important for the bulk production and commercialization of substrates for regular usage. Despite the long history of SERS, flexibility garnered much interest only recently because of easy sample collection from any uneven surface by simple swabbing/swiping etc. Producing uniform, stable, and highly sensitive SERS substrates has been a major obstacle for real-field applications. Therefore, the main task for the SERS community has been to develop the substrates with high sensitivity/reproducibility, long stability, low cost, and easy to handle, as well as flexible for sample collection.

The important results from the literature survey over the last 5–10 years concerning the usage of flexible SERS substrate for various hazardous materials detection is also summarized in this article. A large number of papers have been published in this area. To demonstrate the magnitude of research, a simple search for papers published in the journals and conferences, including the title/keywords/abstract "flexible Surface Enhanced Raman Spectroscopy" or "flexible Surface Enhanced Raman Scattering" or "flexible SERS" as indexed by the Scopus search engine, resulted in typically >100 papers in 2019, >100 papers in 2020 and >40 in the year 2021 alone. The corresponding data obtained is plotted as a bar graph and is shown in Fig. 3. The identification of all the developments and practical applications of flexible SERS studies in various fields will be difficult to be presented in this review. Therefore, we have acknowledged the most important recent review articles and those are listed in the Table 1 below. The readers are suggested to select and pursue the review based on their interest(s). This review is limited to the recent studies (typically during the last 3–4 years) on flexible SERS substrates used in the detection of hazardous materials, rather than including broad discussions on solid SERS substrates (nanostructures on solid targets and metal NPs suspension on the solid platform) and their developments, which is a huge field. This review is warranted because of the extremely rapid developments in the area of different nanomaterials synthesized (for SERS studies including plasmonic and non-plasmonic), novel methodologies developed for incorporating various nanoparticles in different flexible platforms, and detection of diverse analyte molecules.

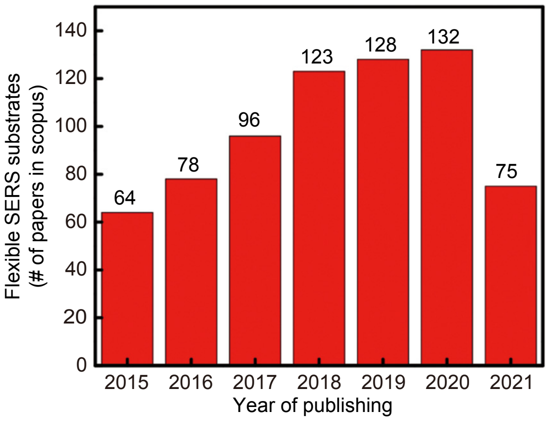

Fig. 3 | Year wise publications on flexible SERS substrates obtained through a search in SCOPUS.

Table 1 | Important review articles on various applications of SERS that have been reported in the last three-years (2019–2021).

S. No.	Author	Review topic	Ref.
1	Zhang et al.	Flexible SERS substrates and recent advances in food safety analysis	ref.[43]
2	Yin et al.	Recent process of 2D materials in SERS	ref.[30]
3	Klapec et al.	2016–2019 published literature on the forensic related molecules and their various detection techniques using SERS	ref.[44]
4	Li et al.	Fabrication and applications of flexible, transparent SERS substrates	ref.[45]
5	Forbes et al.	Developed and challenges of SERS sensor in the detection of inorganic based explosives	ref.[46]
6	Ji Sun et al.	SERS substrate developments and combination with other technologies in on-site analysis using portable Raman spectrometer	ref.[19]
7	Jingjing et al.	Different dimensional (0D, 1D, 2D and 3D) SERS substrates for explosive detection	ref.[47]
8	Shvalya et al.	Plasmonic NPs and 3D plasmonic NSs sensors with biological, medical, military, and chemical applications	ref.[48]
9	To et al.	Explosive trace detection technologies and latest advances	ref.[49]
10	Ren et al.	Qualitative and quantitative analysis; strategies of practical application of SERS substrates	ref.[50]
11	Huang et al.	Paper SERS substrates in food safety	ref.[51]
12	Chen et al.	2D SERS substrates in chemical and biosensing	ref.[52]
13	Dinesh et al.	Flexible sensor fabrication with various printing techniques	ref.[40]
14	Xue et al.	Flexible nanofiber-based substrates fabrication and application	ref.[53]
15	Ogundare et al.	Cellulose-based SERS substrates: fundamentals and principles	ref.[39]
16	Zamora Sequeira et al.	Various methods for the determination of pesticides	ref.[2]
17	Piolt et al.	Key aspects of SERS and application in the biomedical field	ref.[54]
18	Ogundare et al.	Cellulose substrate fundamental, preparation methods, and applications	ref.[39]
19	Lee et al.	Analyte manipulation and hybrid SERS platforms for real-world applications	ref.[55]
20	Xu et al.	Latest advances of flexible SERS substrates in point of care diagnostic in tunable, sample swapping and in-situ SERS detection highlights	ref.[56]
21	Zhang et al.	Electrospinning NPs based material and their sensing application	ref.[57]
22	Restaino et al.	Plasmonic paper SERS substrates-preparation methods and sample collections	ref.[36]

Flexible SERS substrates

A forthright method to achieve the SERS-active substrates is to dry the colloidal NPs (preferably plasmonic) solution on any of the glass/silicon/paper/metal surfaces.[1] Depending on the platform where these NPs/NSs are deposited, the SERS substrates can be classified as either rigid or flexible. Rigid SERS substrates are accomplished via deposition of colloidal solutions on the surface of the glass or silicon or metal sheet and patterned glass/silicon/metal sheets [e.g., metal-insulator-metal structures Au-SiO_2-Au[59]]. Alternatively, flexible SERS platforms can be achieved from the usage of cellulose papers, textiles, thin films, polymers, adhesive tapes[60–64], etc. Both rigid and flexible SERS substrates have their exclusive advantages and disadvantages. Solid SERS substrates usually display better recyclability, signal homogeneity, and higher enhancement factors. However, the cost and sample collection have a considerable impact on daily practical usage of any SERS substrate. Apart from the detection of molecules, flexible substrates have potential in several applications such as fabrication of electronic devices[65] (diodes, transistors, energy storage devices, etc.), food safety[66], cancer screening[67], and pathogens multiplex detection[68], uric acid in human tears[69].

The capabilities of flexible SERS substrates have gained tremendous research interest due to

- Inexpensive fabrication procedures making it possible to prepare large area substrates.
- Easy-to-use nature for on-site detection of a wide range of probe molecules.
- Flexibility in sample collection, i.e., possible to collect the probe molecules/sample directly from any rough surface (e.g., suitcase, bag, table surface, fruit, etc.) with the substrate by simple swabbing/swiping.

The merits of the SERS technique with the portable Raman spectrometer now widely used in national security, food safety, and environmental monitoring.

Recently explosives detection was approached by fabricating various flexible SERS substrates. Liyanage et al[58]. synthesized flexible SERS sensors with an adhesive film (Scotch magic-tape) loaded with Au triangular nanoprisms by simple self-assembly method as shown in Fig. 4. The estimated LOD of TNT, RDX, and PETN was ~900, ~50, and ~50 ppq (parts per quadrillion), respectively. Furthermore, they have also demonstrated direct sampling detection of TNT which was collected from fingerprints by simple swabbing of samples which were

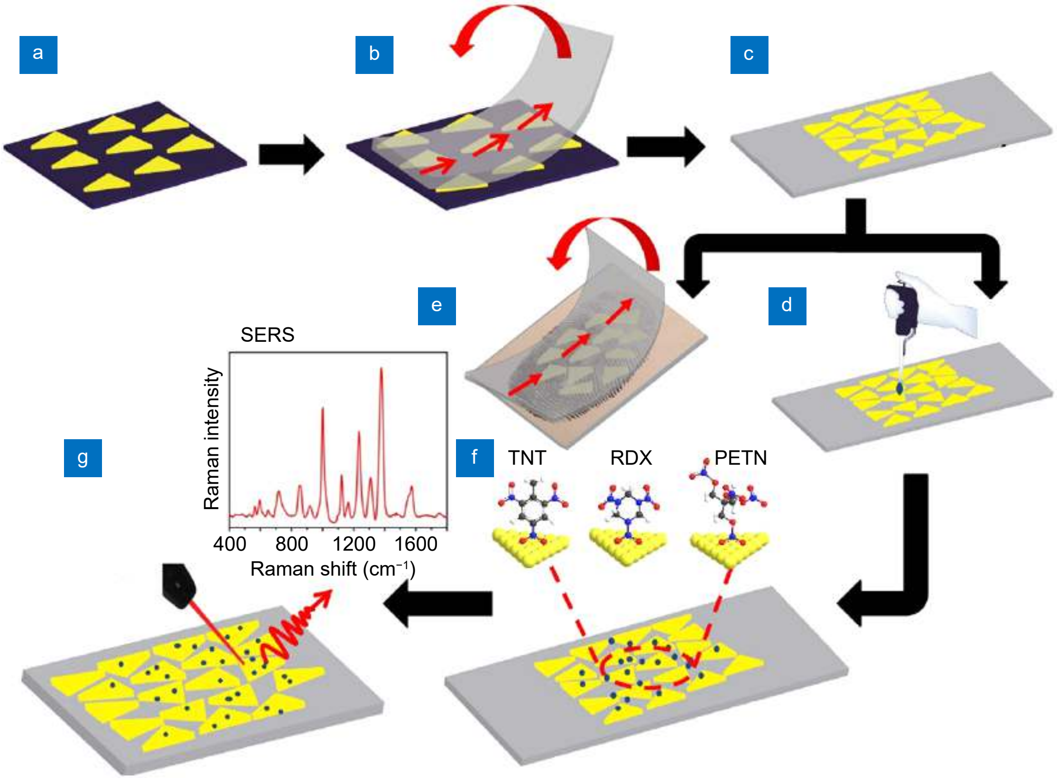

Fig. 4 | Explosive trace detection using flexible SERS substrates detection of TNT, RDX, and PETN using self-assembly triangular nanoprisms on adhesive tape. Figure reproduced with permission from ref.[58], Royal Society of Chemistry.

prepared by placing the thumb onto a series of 10 glass slides. And they successfully proved these flexible SERS substrates have the stability with a “shelf life” of at least 5 months. Gao et al[70]. synthesized light trapping wrinkled nanocones (50–60 nm) flexible SERS substrates using colloidal (polystyrene microspheres-1 μm) lithography and oxygen plasma etching (5 minutes) on polyethylene terephthalate (PET) film followed by 30 nm gold film by electron beam deposition. The optimized wrinkled nanocone 4-ATP labelled flexible substrate was used to detect four explosive molecules RDX, HMX, PETN, and TNT. The TNT residue collection and SERS spectra of TNT residues from the cloth bag by bended to brush collection is followed by 5 min immersion in 4-ATP-labelled AgNPs.

Paper-based SERS substrates

A detailed literature survey revealed that a variety of papers were used (as a base material) for preparing the SERS substrates such as filter paper[71], chromatography paper[72], A4 sized paper[73], tissue papers[74], and different GCM grade papers[75]. The porosity of the paper (which is typically a few μm) will affect the retention of NPs on its surface. There are numerous approaches for the fabrication of paper-based SERS substrates reported in recent literature including physical vapor deposition[76,77], dipping method[67,71], in-situ growth of metal NPs[78,79], hydrophilic wells by wax printing followed by drop-casting of the NPs[80], pen-on-paper technique[73], inkjet printing[72,81], etc.. Some of these techniques of the fabrication of paper substrates, collated from a few recent research reports, is illustrated in Fig. 5. The in-situ synthesis implies soaking of a cellulose paper in metal salts such as $AgNO_3$/$HAuCl_4$ in conjunction with reducing agents (such as $NaBH_4$/citric acid/Tollens agent). These methods later require additional processing such as heating/plasma treatment/rinsing/cleaning. Therefore, these synthesis procedures need multiple cycle processes[82–84]. Dip coating is a unpretentious method in which the NPs have to be first synthesized, then the NPs are deposited on to the paper. However, the NPs loading depends on the absorbance and soaking time of the paper (a comprehensive discussion on the above techniques is provided in ref.[1]). Several recent studies have demonstrated the utility of different approaches for improving the loading [e.g., prior soaking of paper in NaCl, Glycidyl-trimethyl-ammonium chloride (GTAC)][85,86]. The advantage of dip coating/immersion method is its ability to deposit NPs with different shapes, sizes, and compositions on the paper[87–89]. Another popular fabrication method is the inkjet/screen printing, which is a simple method of deposition of NPs on paper using a commercial desktop inkjet printer. The efficacy of the SERS substrate depends on the designing of substrate patterns, which is to preserve the viscosity and surface tension of the NPs ink, and printing cycles to upsurge the density of NPs. Inkjet printing offers easy-to-design complex geometries using a personal computer and it is feasible to print already prepared NPs (by laser-based or chemical methods) and in-situ synthesis is also possible by loading precursor agents in different color ink cartridges[90]. Furthermore, to improve the SERS substrate efficiency and to avoid unwanted spreading of NPs, hydrophobic modification of paper has been exploited before the printing of NPs[91].

Kim et al[92]. used a silicon rubber mask (3 mm diameter and 1 mm thickness) to construct SERS sensor arrays. Gold nanorods (AuNR, L/D: 44±2/10±1 nm) were dispersed on top of RC cellulose with vacuum-assisted filtration method on each well on RC hydrogel. The SERS activity and these AuNR array film was examined as a function of the AuNRs volume (8, 10, 12 and 14 μL) and different drying times (1,2, 3 and 24 hours), and better SERS activity is noticed for 12 μL with increasing drying time. These SERS arry demonstrated the simultaneous detection of multiple hazardous chemicals such as R6G (10 pM), RB, CV, 4-ATP, BPE, thiram (100 fM), tricyclazole, difenoconazole, and mancozeb. And the Multi-SERS spectra of thiram are recorded from each AuNR array on RC film. [i) 10 μM; ii) 1 μM; iii) 100 nM; iv) 10 nM; v) 1 nM]. And also, bending cycle tests were conducted for 500 times. These results show good sensitivity, stability and repeatability of low-cost flexible SERS substrates. Li Xian et al[93]. fabricated cellulose nanocrystal-Ag NPs embedded filter paper SERS substrate via in situ reduction. These CNC –Ag paper substrates were modified by soaking in dodecyl mercaptan at different concentrations ranging from 10^{-4} to 10^{-18} g/mL. The concentration was optimized as 10^{-12} g/mL by performing contact angle and SERS measurements. Finally, the optimized SERS substrate was used to detect phenylethanolamine A and metronidazole with a LOD of 5 nM and 200 nM. Lan et al[74]. reported the inkjet-printed paper-based semiconducting (MoO_{3-x}) SERS substrates to detect CV and MG on the fish surface by swabbing. Previously, our group presented a systematic study[94] on the

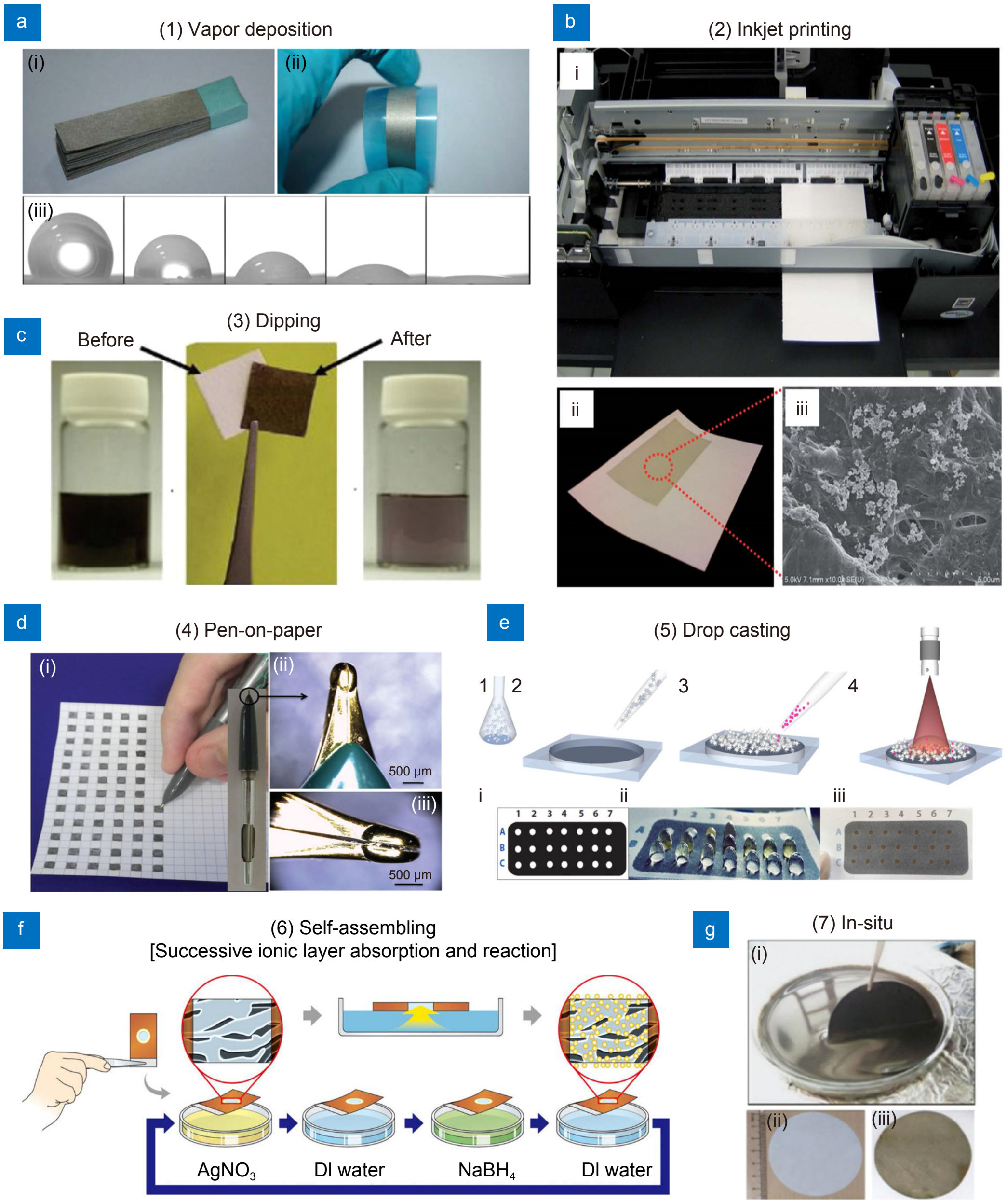

Fig. 5 | Various fabrication techniques used for paper-based SERS substrates. (**a**) Vapor deposition. (**b**) Inkjet printing. (**c**) Dipping. (**d**) Pen-on-paper. (**e**) Drop-casting on hydrophilic wells. (**f**) Self assembling. (**g**) In-situ reduction. Figure reproduced with permission from: (a) ref.[77], (b) ref.[72], The Royal Society of Chemistry; ref.[71], American Chemical Society; (d) ref.[73], John Wiley and Sons; (e) ref.[80], Springer Nature; (f) ref.[84], (g) ref.[79], American Chemical Society.

fabrication of versatile low-cost FP flexible SERS substrates loaded with salt-induced aggregated Ag/Au NPs. The SERS substrates were subsequently prepared by soaking the FP in aggregated NPs by simple addition of different concentrations of NaCl (1 to 100 mM). The detailed SERS measurements were indicated that the Ag/Au NPs with 50 mM NaCl concentration is the optimal SERS performance. This optimized FP with aggregated Ag/Au NPs were used detect four adsorbed molecules MB-5 nM, PA-5 µM, DNT-1 µM, and NTO-10 µM using portable Raman spectrometer. The schematic of FP SERS preparation (a) the SEM image of FP (b) without and (c) with NPs and the SERS spectra of explosive molecules (right side) are shown in Fig. 6.

Lin et al[95]. reported the PDMS assisted paper based SERS platform for the on-site monitoring of food safety. Firstly, Au@Ag nanorods (NRs) are synthesized using seed mediated growth, and are deposited on filter paper

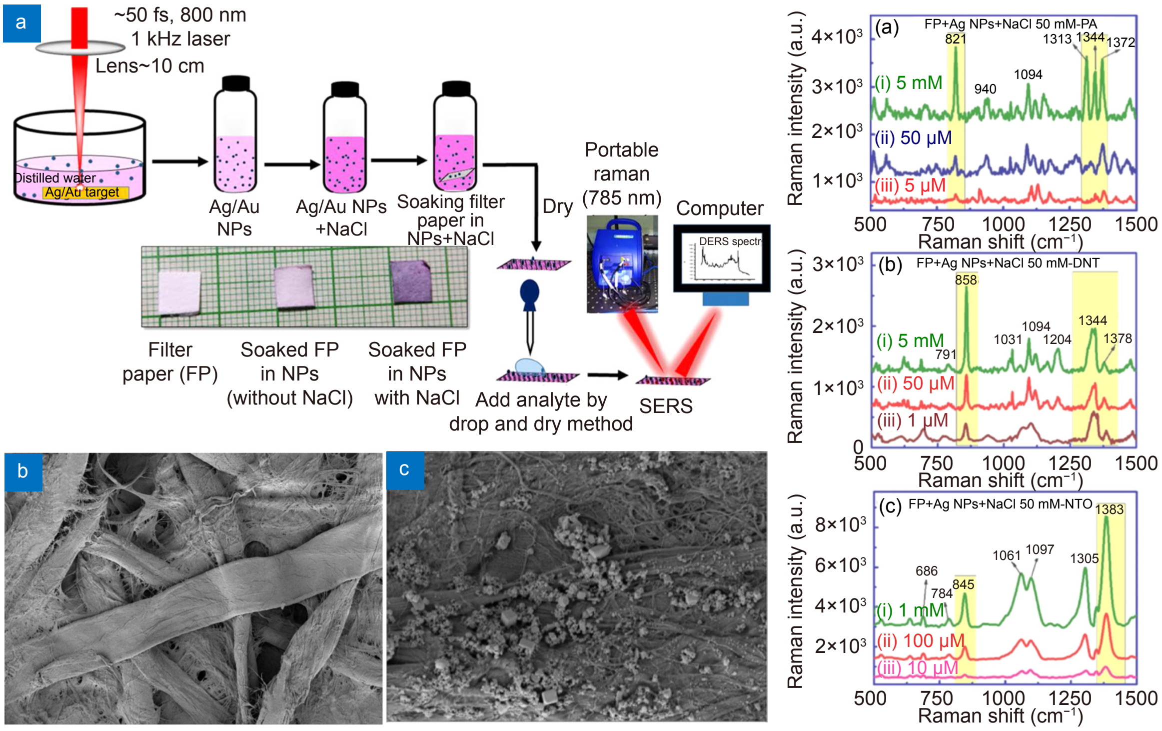

Fig. 6 | Filter paper based SERS substrate by aggregated Ag/Au NPs for explosive molecule detection (Left side) (**a**) schematic of substrate preparation (**b**) and (**c**) FESEM images of bare filter and aggregated Ag NPs (Right side) SERS spectra of (a) PA (b) DNT (c) NTO using FP with optimized aggregated Ag NPs. Figure reproduced with permission from ref.[94], American Chemical Society.

through self-assembly technique. Finally, dual functional SERS platform was made via side of the paper with the NPs affixed onto PDMS using polymethyl methacrylate (PMMA) tape, as the schematic shows in Fig. 7(a). The SERS platform optimized by Au@Ag NRs with 1 to 6 layers were also assembled on the filter paper, and SERS measurements (CV) demonstrated that the Raman intensity of the probe molecule gradually decreases as the number of layers increases. The optimized monolayer SERS paper-based PDMS-assisted platform was used to detect thiram (0.75 ppm) on the surface of orange by just simple wiping and the presence of PDMS enables higher performance with better sensitivity of SERS. Further, various concentrations of thiram on orange surface (from 0.5 ppm to 50 ppm) and the concentration versus intensity Langmuir adsorption for the Raman spectra are shown in Fig. 7(b).

Polymer-based SERS substrates

Nanofiber mats

Electrospinning is a method of translation of polymeric solution/melt (with or without additives) into solid nanofibers by applying the electric field[1]. The electrospun nanofiber films are identical to paper substrates in many aspects. For example, they have similar flexibility, porosity, and a high surface area. Moreover, their morphology, thickness, porosity, etc. (of the nanofiber films) can be varied by judiciously choosing the experimental parameters (i.e., solution parameters, process parameters, and ambient parameters)[53,96–98]. The concentration of polymer solution being used demonstrates an essential role in the electrospun fiber fabrication. At very low concentrations of the polymer solution, electrospraying occurs instead of electrospinning. Therefore, micro/nanodroplets are deposited on the collector drum. With a slight increase in polymer solution concentration, a mixture of microbeads and fibers has been observed[1]. Smooth nanofibers are observed at an appropriate concentration depending on the polymer molecular weight. If the concentration is too high, nanofibers will not be formed, and only micro-ribbons will be observed[1]. Therefore, with an increase in the concentration of the polymer solution, the obtained fiber diameter will increase. Usually, the viscosity and surface tension of the solution can be modified by altering the concentration of the used polymer. At a very low viscosity or surface tension, continuous and smooth fibers cannot be attained. If the viscosity of the polymer solution is very high, it results in the hard ejection of polymer jet from the syringe

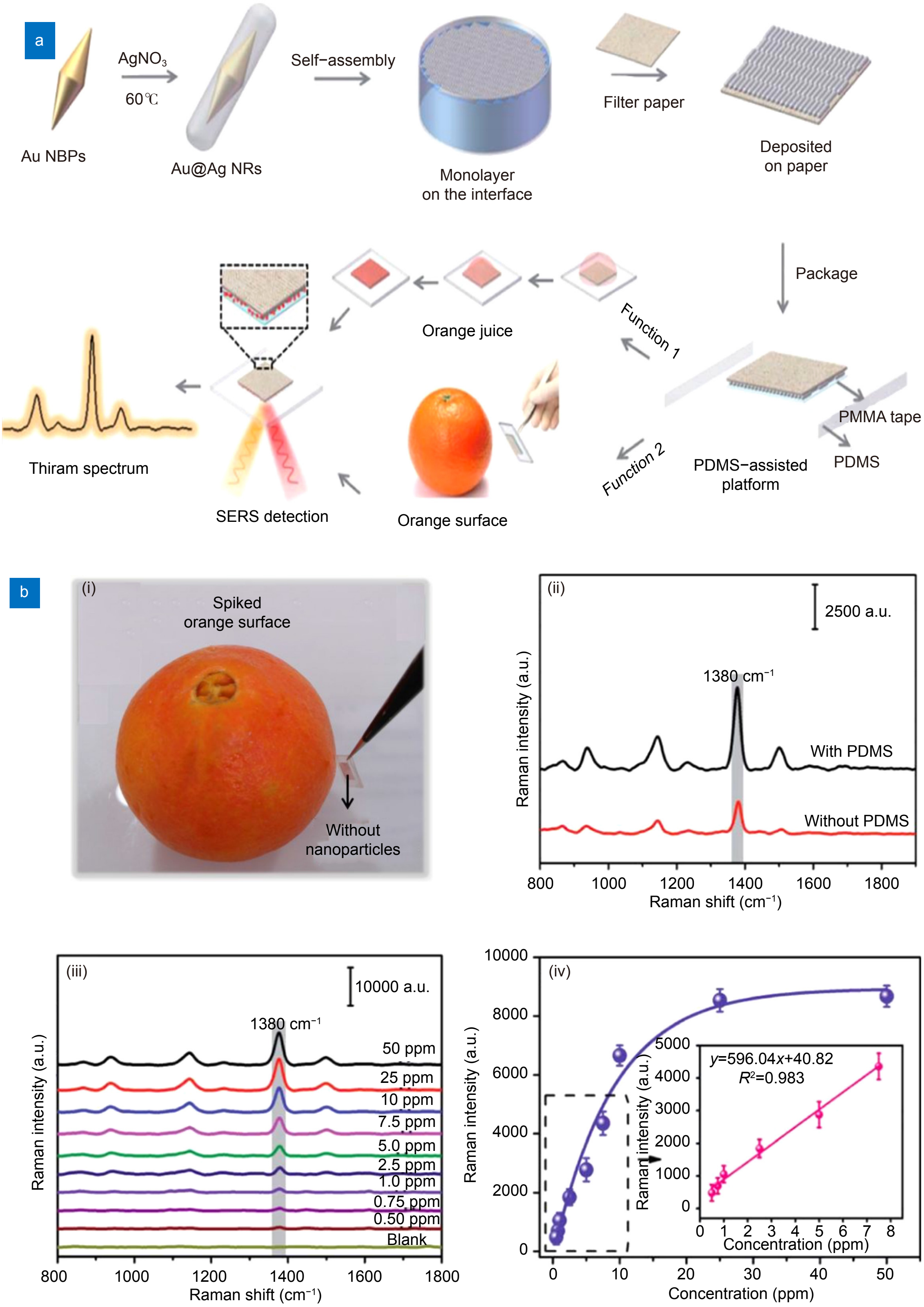

Fig. 7 | (**a**) A schematic of the synthesis of dual-functional PDMS-assisted paper-based SERS platform. (**b**) (i) The photograph of a sample collection from orange surface. (ii) A comparison of SERS spectra of CV with and without PDMS. (iii) SERS spectra of different concentrations of thiram (0.5−50 ppm). (iv) The peak intensity at 1380 cm−1 of thiram in orange juice as a function of the spiked sample concentration. Figure reproduced with permission from ref.[95], Royal Society of Chemistry.

needle. The polymer molecular weight also affects the fiber morphology as a decrease in the molecular weight tends to form more beads rather than smooth fibers. Husain et al[99]. analyzed the fiber morphology of PLGA [poly (lactic-co-glycolic acid)] in acetone with a varying concentration between 2 and 25 wt%. At low concentration (2–4 wt%), a mixture of particles and beads-on strings are observed, and at high concentration (20–25 wt%), only fibers are obtained. The fiber morphology can be tuned with the processing parameters such as the applied voltage for the electrostatic force, flow rate, nozzle-collector distance, fiber collector humidity, and temperature, etc. Recently, Wan et al.[100] reported SiO_2 electrospun nanofiber loaded with Ag/Au nanoparticles SERS substrate with high sensitivity -10^{-11} mol/L, stability – 60 days, repeatability for various molecules (S. aureus, thiram, 4-MPh, and 4-MPA), and the schematic is illustrated in Fig. 8.

The SERS performance of nanofiber depends on the properties of

- nanofibers (polymer nature, fiber diameter, the morphology of the nanofibers, and spinning time, etc.) and
- nanoparticles[101] (material type, size, shape, composition, and density), etc.
- Decoration of NPs on the fiber[102,103] (within the fiber, the surface of the fiber, etc.)
- The loading of NPs on the nanofiber mat leads to the NPs assembly with extremely small spacing providing scope for abundant hot spots. These play a crucial factor in SERS response.

Electrospinning polymer fibers can be used as SERS substrates by loading plasmonic NPs; similar to paper substrates, several methods are reported for embedding metal NPs onto the electrospun polymer films like dispersion of metal precursor and pre-mixing of metal NPs into the polymer solution and surface medications after electrospinning. Chamuah et al[104]. demonstrated the Au deposition after electrospinning PVA nanofiber. Recently, Motamedi et al[105]. added laser-ablated Au NPs in Polyvinylidene fluoride (PVDF) solution before electrospinning. Zhang et al[106]. performed different trials on the addition of Au nanorods in the PVA solution before electrospinning. Zhang et al[107]. have performed a detailed study on fabrication of electrospun nanofibrous surface decorated with Ag NPs. Amidoxime surface-functionalized polyacrylonitrile (ASFPAN) nanofibrous membranes surface-decorated with Ag NPs using electrospinning followed by the seed-mediated electroless plating. A series of SERS substrates were prepared by altering the reaction time (1, 2, 3, 4 and 5 minutes) and stirring conditions (stirring and non-stirring) during the electroless plating deposition of Ag NPs. The change in the size, shape, and aggregation of Ag NPs on the surface of nanofibrous membrane and their effect on SERS efficiency were evaluated. The best SERS sensitivity was noticed for ASFPAN-Ag NPs nanofibrous membrane at 3 minutes under non-stirring condition, the corresponding reflectance, SEM and TEM images shown in Fig. 9. These optimized SERS substrates detect 10 ppb R6G and 4-MBA.

Recently flexible polymer-based (PDMS[108], PMMA[109], PET[110], PVDF[111,112], etc.) SERS substrates have gained interest from various research groups. Wang et al[113]. have synthesized the sandwiched Au@Ag NPs [between

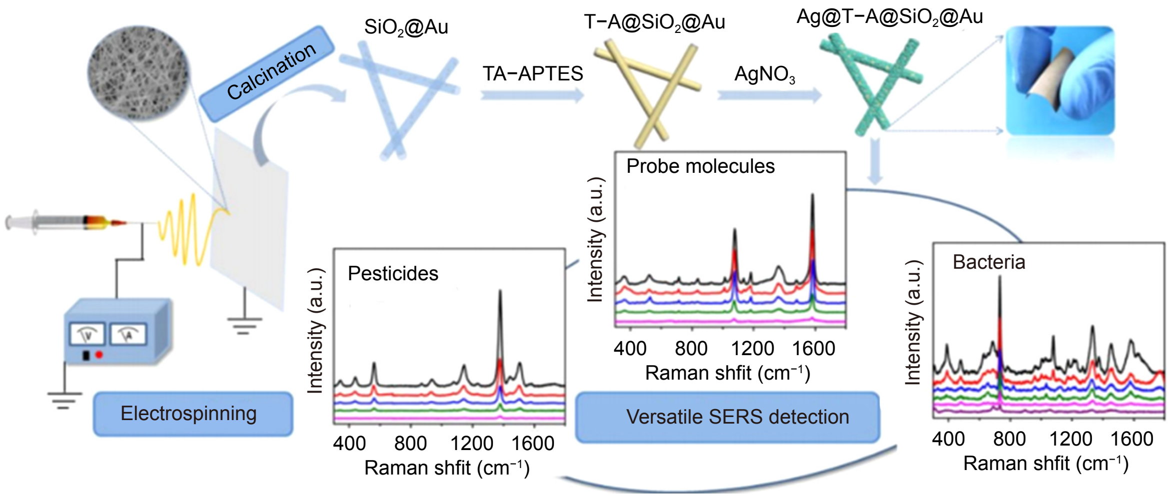

Fig. 8 | Fabrication of flexible SERS substrates for Ag@T-A@SiO_2-Au nanofibrous substrates. Figure reproduced with permission from ref.[100], under a Creative Commons Attribution 4.0 International License.

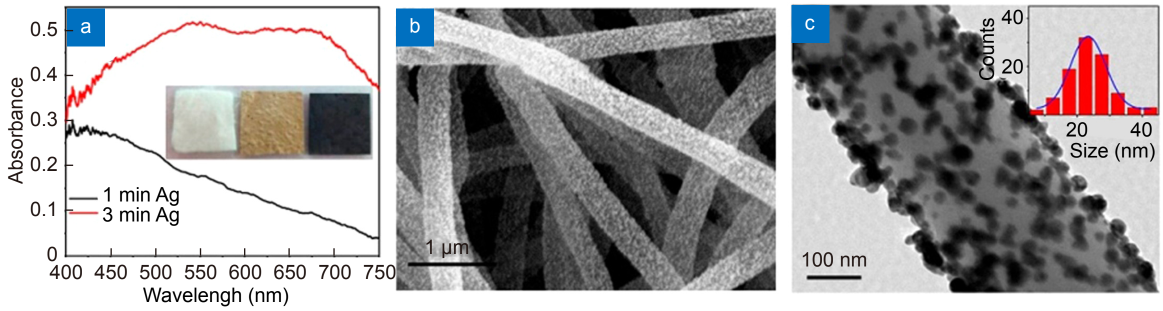

Fig. 9 | (**a**) Reflectance spectra of the ASFPAN nanofibrous membranes with Ag NPs; Photographs of three nanofibrous membranes (PAN, AS-FPAN, and ASFPAN-Ag NPs) are shown in the inset. (**b**) SEM image and (**c**) TEM image of ASFPAN nanofibers (3 min). Inset in (c) shows the size distribution of Ag NPs.[107], American Chemical Society.

adhesive acrylic polymer tape and polyethene terephthalate (PET)] film using the self-assembly method. Here, PET film was used to protect the Au@Ag NPs array from environment for long-term stability (60 days). While performing the SERS measurements, the protection PET film was peeled off carefully, and the T/Au@Ag substrate was utilized for sensing CV-1 nM with a LOD of ~9×10^{-10} M. These flexible T/Au@Ag substrates were further investigated for realistic applications like thiram residues extracted from the peel of apple, tomato, and cucumber. Zhang et al[114]. reported low cost large area high-throughput nanostructured polymer flexible SERS substrate, the schematic shown in Fig. 10(a). These were prepared in three steps (1) preparation of anodic aluminum oxide (AAO) mold (2) formation of polymer nanostructure using roll-to-roll ultraviolet (365 nm,

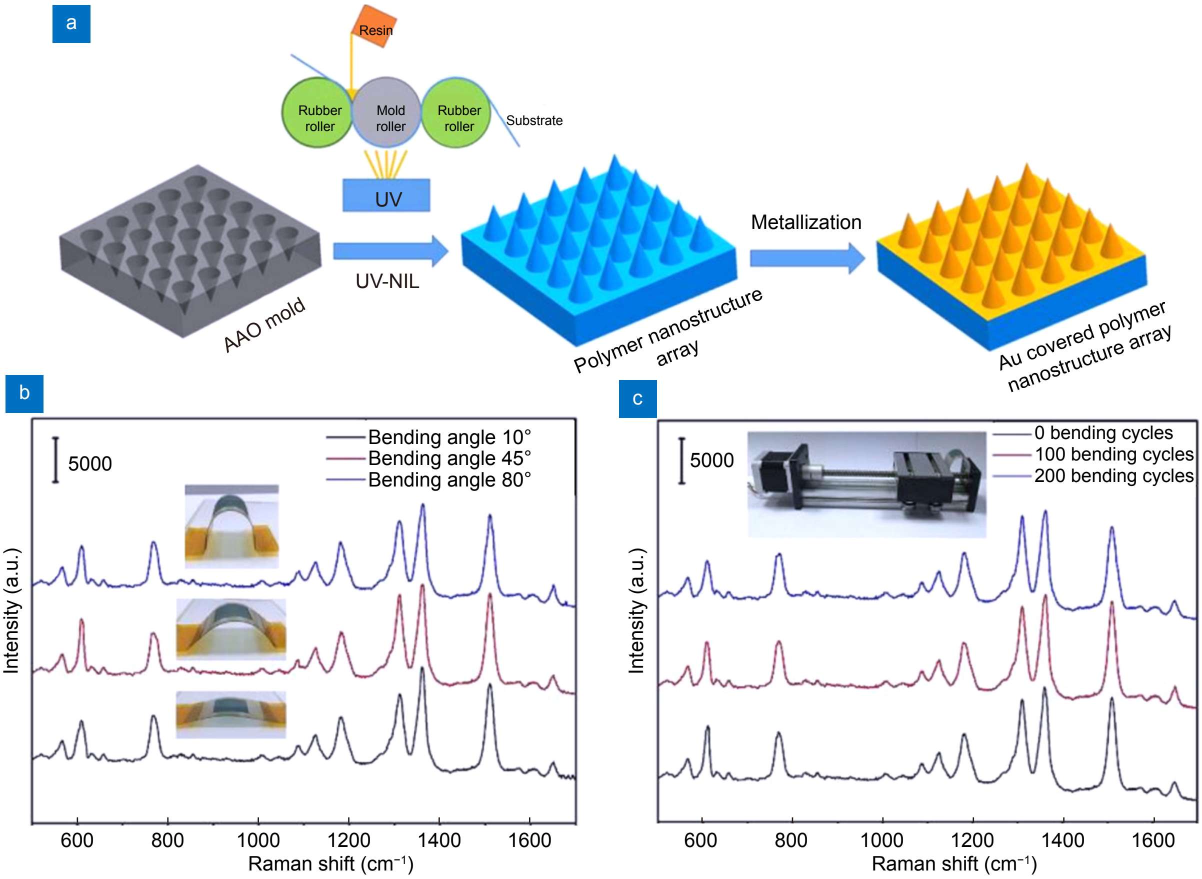

Fig. 10 | (**a**) Schematic diagram representing the fabrication process of Au covered polymer nanostructure arrays using roll-to-roll ultraviolet nanoimprint lithography (R2R UV-NIL) technique (**b**) and (**c**) SERS spectra of R6G from 30 nm Au coating flexible substrate at different bending angles and bending cycles, respectively. Figure reproduced with permission from ref.[114], under a Creative Commons Attribution 4.0 International License.

40 mW/cm^2) nanoimprint lithography (R2R UV-NIL) technique (3) Au coating on polymer nanostructures by ion sputtering. Here, the effect of Au coating thickness 15, 30, 45, 60 nm on SERS was investigated by varying the sputtering durations of 90, 180, 270, and 360 s, respectively. The SERS performance was assessed with probe molecule R6G and it was noticed 30 nm Au coating substrate shows the highest Raman signal with EF 1.21×10^7. Subsequently, the flexible effect on SERS under some mechanical deformations was investigated with different bending angles (10°, 45° and 80°) and bending cycles (0, 100 and 200). In the SERS signal intensity and peak positions plot, there was also no obvious difference with the corresponding spectra shown in Fig. 10(b) and 10(c).

Fang et al[115]. recently reported polymer [polytetrafluoroethylene (PTFE)] based flexible SERS substrates fabricated using versatile femtosecond [290 fs, 1030 nm, 200 kHz, 1500 mW] laser direct writing technique. 3D patterned polymer micro-/nano-structures were obtained and were subsequently coated with Ag using thermal evaporation technique. These flexible SERS substrates were used to detect R6G at a concentration of 10^{-7} M. The advantages of the fs laser processing were its simplicity, high-speed, and possibility of preparing large area substrates, which leads to bulk sample preparation for practical applications. Over the last few years, our research group at the University of Hyderabad, India has successfully fabricated a variety of SERS substrates using fs laser ablation of bulk targets such as Au[116–118], Si[119,120], and Ag[121], and optimized them by varying the various laser parameters. In future, we aim to prepare low-cost flexible SERS substrates using fs laser pulses for easy sample collection and real-world applications. The nanocolloids and nanostructures obtained with fs laser ablation (in liquids) technique are ubiquitous and versatile. The recent developments in this area of research have proven that these can now be produced in large quantities.

Textile based SERS substrates

The textile fabrics have also been investigated as an attractive SERS substrate (akin to paper and electrospun fiber substrate) because the fabric is naturally strong, flexible, soft, and a lightweight material. In textiles, various materials are available such as cotton, wool, silk, etc.. Comparable to other flexible substrates, the loading of NPs can be done in two ways, i.e., in-situ synthesis [soaking in different metal salts] and direct deposition of NPs [anisotropic silver nano-prisms and nano-disks to wool fabric has been reported recently[122]]. Liu et al[123]. synthesized silk fabrics SERS substrate by soaking in $HAuCl_4$ (0.1–0.6 mM, 50 mL) for 30 minutes, followed by heating and cleaning. These Au NPs loaded silk fabrics were used to detect CV, 4-MPy, and PATP. Chen et al[124]. fabricated Ag-based cotton fabric by soaking in $AgNO_3$ (50–250 mM) followed by reduce-drying (30 °C for 30 min) process. The fabric soaked in 200 mM demonstrated better sensitivity (10^{-12} M) with 20% reproducibility and 57 days stability in the detection of p-Aminothiophenol. Furthermore, these fabric substrates are having other applications UV protection, antibacterial, and self-cleaning[125,126]. Gao et al[127]. reported wash free metallic textile utilization as flexible SERS substrate for the detection of fungicide. They fabricated Ag-coated cotton fabric using magneton sputtering and the SERS performance was optimized with Ag film thickness as 100 nm from the series of thickness such as 50, 100, 150 and 200 nm on cotton fabric using MB as a probe molecule. The optimized 100 nm Ag-cotton fabric substrate used to detect MB at a low concentration of 10^{-12} M, for the real time usage they detected thiram on 10 ppb. Additionally, they have shown the reusability of these substrates by alternative usage of MB and MG, this dye droplet was removed by a simple stream of air. Lu et al[128]. synthesized carbon fiber cloth substrate loaded with 3D Ag nanodendrites by electrochemical deposition. SERS substrate preparation was optimized by studying the effect of deposition voltage (1.1, 1.2, and 1.3 V) and deposition time (80, 120, 160, 200, 240 s), and the optimal SERS substrate was selected by observing nanodendrites morphology and SERS efficiency as under a voltage of 1.3 V and with deposition time of 160 s, shown in Fig. 11. They reported the detection of 1 pM CV and simultaneous detection of three other molecules (4-MBA –5 ppm, DDTC –5 ppm, and thiram –5 ppm). They presented the real time detection data (SERS spectra) of thiram (5 ppm) and MG (5 ppm), respectively, on superhydrophobic Ag-NDs/carbon fiber cloth substrate. Further, they also demonstrated the detection of thiram and MG simultaneously in real lake water using superhydrophobic Ag NDs/carbon fiber cloth substrate. Zhang et al[129]. recently reported the synthesis of non-woven (NW) fabric based SERS substrate and utilized for carbaryl pesticides trace detection on fruits surfaces. NW@polydopamine (PDA) @AgNPs fabrics SERS substrates were fabricated by in-situ growth using mussel-inspired PDA molecules. The

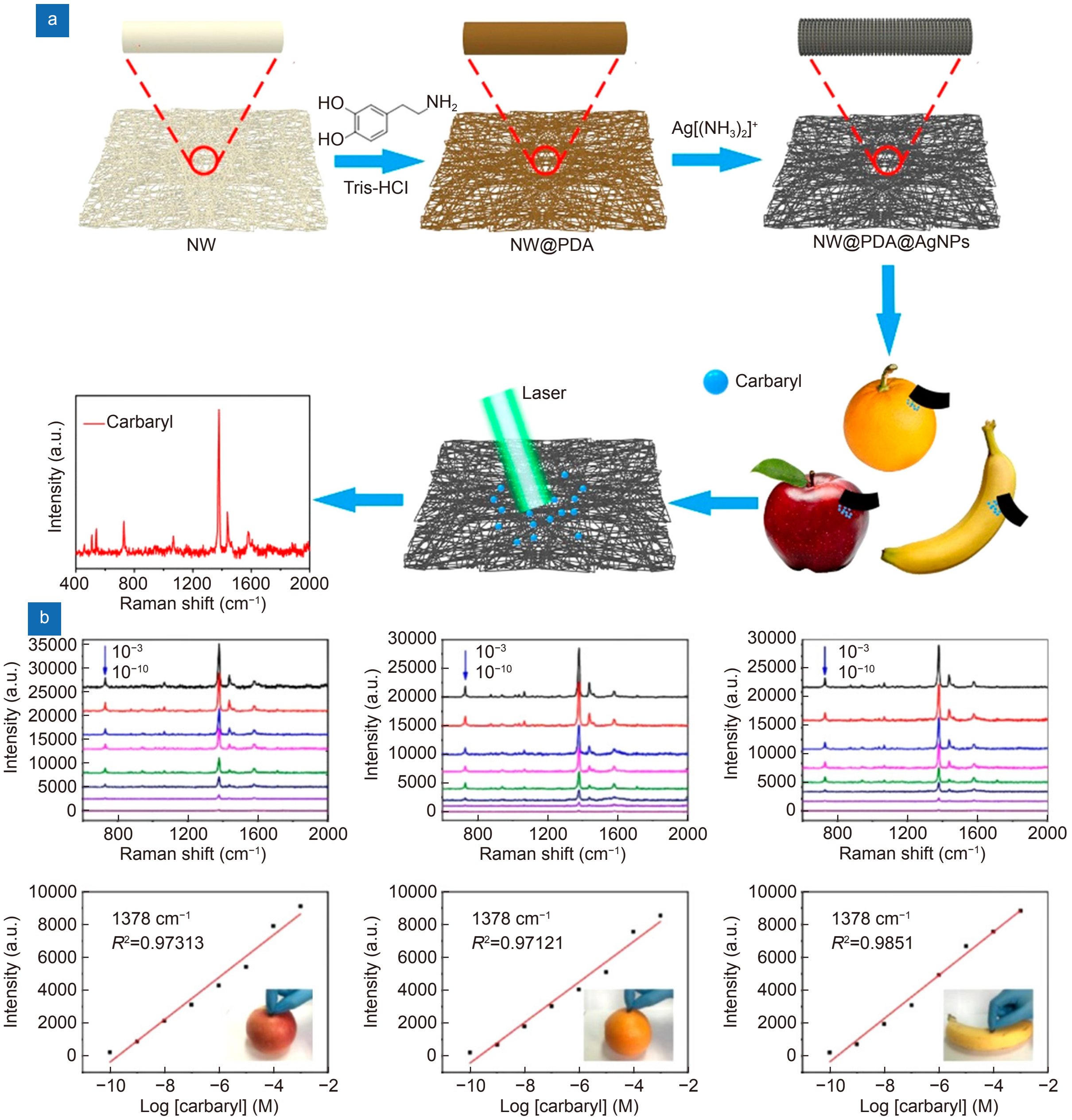

Fig. 11 | (**a**) Schematic of flexible non-woven fabric based substrate and the (**b**) SERS spectra of carbyl on apples, oranges, and bananas surfaces. Figure reproduced with permission from ref.[129], under a Creative Commons Attribution 4.0 International License.

schematic of the fabrication of flexible NW@PDA@Ag NPs substrate and their utilization by simple swabbing method are illustrated in Fig. 11(a). The substrate was optimized by monitoring the immersion time of NW@PDA fabrics in the $[Ag(NH_3)_2]^+$ solution. With increasing the immersion time from 4 hours to 12 hours, the amount of Ag NPs on fabric was increased, and the superior SERS signal was noticed for 12 hours. The optimized flexible NW@PDA@Ag NPs substrates were subsequently utilized to detect the sprayed diluted carbaryl on the surfaces of apples, oranges, and bananas. The collected SERS spectra of carbyl with concentrations ranging from mM to pM are shown in Fig. 11(b). This is a rapidly growing area of research and has strong potential in the preparation and utilization of flexible SERS substrates for detection of hazardous materials. Different plasmonic nanoparticles (sizes, shapes, preparation methods, concentrations etc.) need to tested and methods optimized with these textiles before we can think of any practical application.

Table 2 summarizes the most important details of recently reported flexible SERS substrates including their preparation methods, materials used in those studies, and the sensitivities achieved. Such data is extremely im-

Table 2 | Summary of the recent flexible SERS substrates, their preparation methods, materials used, and the sensitivities achieved (2014-2021).

Flexible substrate type	Hazardous material type studied	Method used	SERS active material	Molecules investigated - sensitivity	Ref.
Paper/Cellulose	**Explosives**	Inkjet printing	PABT modified-Ag NPs-A4 paper	TNT- pM	ref.[132]
		In-situ	Ag NPs in agarose film supported on filter paper	TNT- 10^{-8} M	ref.[78]
		Immersion	Ag nano triangles-filter paper	PA- 10^{-6} M p-ATP- 10^{-8} M	ref.[88]
		Soaking	Aggregated Ag/Au NPs-filter paper	PA- 5 μM DNT- 1 μM NTO- 10 μM	ref.[94]
		Drop casting	Star-shaped Au NPs	PA-5 μM	ref.[133]
		Reduction	Ag Nanostructures- filter paper Whatman 42	Urea nitrate- 10^{-6} M CV- 10^{-8} M	ref.[134]
	Drugs	Inkjet printing	Ag- chromatography paper	Organophosphate malathion –413 pg, Heroin –9 ng, Cocaine –15 ng	ref.[135]
		Plasma assisted chemical deposition	Au-Whatman filter paper grade 1	Cocaine- 1 ng/ml	ref.[136]
	Dyes	In-situ	Ag NPs-polydopamine -Filter paper	R6g- 10^{-10} M MG residue on Fish scales- 0.04635 pg/cm^2, Crab shells- 0.06952 pg/cm^2 and Shrimp skins- 0.09270 pg/cm^2	ref.[137]
		Inkjet-printing	MoO_{3-x} nanosheets on Chromatographic paper, printing paper, filter paper	R6g- 10^{-7} M CV- 10^{-6} M and MG- 10^{-6} M on fish surface	ref.[74]
		In-situ	Au-filter paper (Advantec #1)	MG-damped fish– 10 ppb	ref.[138]
	Pesticides	Silver mirror reaction	Ag- filter paper	Thiram- 10^{-7} M	ref.[139]
		Pen on paper	Au NPs (15–120 nm); Au NRs (50 nm long, 14 nm thick); Ag NPs (50-80 nm) –A4 paper, Filter paper	Thiabendazole < 20 ppb	ref.[73]
		Airbrush spray method	Ag NPs -glass fibre paper	Enoxacin & Enrofloxacin- 10^{-5} M	ref.[140]
		Printing	Au@Ag 30 nm Au core & 7 nm Ag shell -filter paper	Thiram- 10^{-9} M	ref.[141]
		Screen printing	Ag NPs/GO- paper	Thiram 0.26 ng cm^{-2} Thiabendazole 28 ng cm^{-2} Methylparathion 7.4 ng cm^{-2}	ref.[142]
		Immersion followed by APTMS	Ag NPs-PDMS sponge	Triazophos 0.79 ng Methyl Parathion 1.58 ng	ref.[143]
		Vacuum-assisted filtration	AuNPs- cellulose nanofiber	Thiram- 1 pM Tricyclazole- 10 pM	ref.[144]
		In-situ	Au NPs-pseudo-paper	Thiram- 1.1 ng/cm2	ref.[145]
		Laser techniques	Au/Ag film-print paper	Fungicide mancozeb (Dithane DG) and insecticide thiamethoxam (Aktara 25 BG)	ref.[146]
		Immerson in NaCl solution for 5 min +dip-coating	Ag NPs- filter Paper	Melamine- 1 ppm Thiram- 1 ppm	ref.[147]

Table 2 (Continued)

Flexible substrate type	Hazardous material type studied	Method used	SERS active material	Molecules investigated - sensitivity	Ref.
		Immersion	FP-Au NPs	Methyl parathion- 0.011 μg/cm^2	ref.[148]
		In-situ	Nanocellulose fibers-Ag NPs	Thiram- 0.05 ppm Thiabendazole- 0.09 ppm, MG 0.0014 ppm Enrofloxaci- 0.069 ppm	ref.[149]
		Silicon rubber mask and a vacuum filtration	Au NRs -cellulose hydrogels	Thiram- 100 fM	ref.[92]
		Drop casting	Quartz paper/Cellulose nanofiber/ mixture (Ag NPs+Au NSs)	Ferbam on kale leaves (50 μg/kg)	ref.[150]
		Vacuum filtration	Cellulose nanofibers-Au NPs	Thiram- 10^{-8} M	ref.[151]
		Drop casting, inkjet printing	Au NPs-Whatman 44 FP	Benzenethiol chemical aerosol Pyridine	ref.[152]
		Vacuum filtration	Glass-fiber filter paper-Ag NWs coupled with polymerase chain reaction (PCR)	DNA	ref.[153]
		Electrochemical deposition	Mesoporous Au film@Ag NWs@cellulose nanofiber paper	R6g - 100 fM Thiram - 10 fM 2-naphthalenethiol-1 ppb	ref.[154]
		Self-assembling	Cellulose nanofibers - Ag@DNA/PDA (polydopamine)	Rhodamine 6G. Thiamethoxamon- 0.003 mg/kg.	ref.[155]
Cotton buds	**Antibiotics**	In situ reduction	Ag NPs-cellulose nanocrystals-Filter paper	Phenylethanolamine A-10^{-9} M Metronidazole- 10^{-7} M	ref.[93]
	Explosives	Self-assembly & In situ	Ag NPs-cotton swab	2,4 DNT- 5 ng	ref.[156]
	Pesticides	Soaking, freezing, and drying	Ag NPs-chitosan foam	Triasophols Methidathion Isocrabophos	ref.[157]
		Dipping & drying	Ag NPs-cotton swab with NaCl	Thiabendazole (TBZ), thiram, TBZ + thiram	ref.[158]
3D- sponge	**Explosives**	In situ	Ag NPs -polyurethane sponge	Perchlorates- 0.13 ng CChlorates- 0.13 ng Nitrates- 0. 11 ng	ref.[159]
Nanofiber mat	**Pesticides**	Electrospinning	Au coated PVA nanofiber	Deltamethrin- 0.33 mg/kg Quinalphos- 0.28 mg/kg Thiacloprid- 0.26 mg/kg	ref.[104]
	CWA simulants	Electrospinning	Au NPs –PVA nanofiber	Methyl salicylate	ref.[160]
	Dyes	Electrospinning	Ag NPs-PVA nanofiber	R6G-10^{-5} M	ref.[161]
		Electrospinning and in-situ	Ag NPs-Polyimide (PI) nanofabric	p-Aminothiophenol (p-ATP)- 10^{-14} mol/L),	ref.[162]
Fabric	**Pesticides**	Self-assembly/in-situ	Ag NPs- non woven fabric	Isocarbophos Sumicidin Phosgene	ref.[163]
		Dip coating	Triangular Ag nanoplates-Cotton fabric	Carbaryl- 10^{-5} M	ref.[164]
		In situ	Polydopamine mediated Ag-Au NPs – cotton fabric	Carbaryl- 10^{-6} M	ref.[165]
		Magneton sputtering	Ag NPs-cotton fabric	Thiram - 1 ppm	ref.[127]
		Magnetron sputtering	Ag-polyester fabric	R6G on cucumber, MG and Thiram	ref.[166]

Table 2 (Continued)

Flexible substrate type	Hazardous material type studied	Method used	SERS active material	Molecules investigated - sensitivity	Ref.
		Photochemical deposition (254 nm)	Ag NPs on TiO_2 coated polyester fiber membranes	Sodium saccharin in soft drinks- 0.3 mg/L, (cola and sprite)	ref.[167]
		In-situ growth	Ag NPs-Cotton fabrics	PATP-10^{-8} M	ref.[168]
		Vacuum evaporation	Ag coated (10 nm) nylon fabrics	PATP-10^{-9} M Thiram on cucumber surface-10^{-7} M	ref.[169]
Polymers	**Dyes**	Vacuum thermal evaporation and high-temperature annealing	Ag NPs-carbon fiber cloth	R6g- 10^{-14} mol·L^{-1}	ref.[170]
	Explosives	Oriented stacking and in-situ	Ag and Au–Ag nanoplates- PET	TNT- 10 nM RDX- 10 nM	ref.[171]
		Self-assembling	Au triangular nanoprisms on adhesive film (Scotch magic-tape)	TNT- 900 ppq RDX- 50 ppq and PETN- 50 ppq	ref.[58]
		Incubated overnight followed by thorough rinsing drying	Au NPs,Au NRs and Au NCs on elastomeric film (PDMS)	TNT vapor	ref.[172]
		Gravure printing	Ag NPs-PET	DNT vapor	ref.[173]
		Sol–gel method and magnetron sputtering	Ag NPs-Porous silica aerogels	NTO- 7.94×10^{-10} M	ref.[174]
		UV lithography and Au deposition	Ag NPs-Au coated - nanowrinkled zigzag micropattern on PDMS layer	TNT- 10^{-13} mol·L^{-1} TNT residue(10^{-9} mol·L^{-1}) on cloth bag	ref.[175]
	Dyes	Electron-beam evaporation-uniaxial stretching	Stretched Ag coated poly(ε-caprolactone) film	MG-green mussel surface- 0.1×10^{-6} M	ref.[176]
		Pyramid Si template	MoS_2/AgNPs/inverted pyramidal PMMA	R6G+MG	ref.[177]
		Pyramid Si template	GO/Ag NPs/ pyramidal PMMA	MG on shrimp	ref.[178]
		Ar plasma etching and Au evaporation	Worm-like Au NSs – PET film	R6G-10^{-9} M	ref.[179]
		Self-assembly and in situ chemical reduction	Raspberry-like polyamide@Ag hybrid nanoarray film	R6g-10^{-14} M Adenosine- 10^{-9} M	ref.[180]
	Pesticides	Drop-dry method	Au NPs (25 nm) - adhesive tape	Parathion-methyl- 2.60 ng/cm^2 Thiram 0.24 ng/cm^2 Chlorpyrifos 3.51 ng/cm^2 on apples, oranges, cucumbers, and green vegetables surfaces	ref.[181]
		Spin coating and manual peeling	AgNP@AgNW network-PDMS	Thiram (0.1μM) on a leaf surface and MG (0.1μM) on a living fish scale	ref.[182]
		Paste and peeling of self-assembled NPs from Si	Adhesive acrylic polymer tape and polyethene terephthalate (PET) film (T/Au@Ag/PET)	Thiram on apple, tomato, and cucumber peels (5 ng/cm^2)	ref.[113]
		Seed mediated	Gold nanobush+PDMS	Thiabendazole (TBZ) on cherry – 0.64 ng/ml Carbaryl TBZ+Carbaryl	ref.[183]
		Femtosecond laser induced plasma assisted ablation	Ag NPs and Au NPs FEP (fluorinated ethylene propylene)	Thiram on apple- 7.96 ng/cm^2	ref.[184]
		Drop casting	Ag NS with spikes-adhesive tape	Phosmet & carbaryl on apple-surface 10^{-7} M	ref.[185]

portant since the developments are occurring at a rapid pace and it is imperative to identify the strengths and weakness of each of these methodologies to come up with a viable and practical technique for making robust flexible SERS substrates. These flexible SERS substrates find niche applications in the detection of various hazardous materials in Defence, food, and environmental safety issues. Sensitivity estimations are reported in various parameters such as Molar (M), parts per billion (ppb), nanogram (ng), ng/cm^2 and mg/kg. For example, in case of Thiram molecule (molecular weight of 240.44) 10 ppb is ~0.42 nM which is equivalent to ~1 pg in 10 μL; 1 ppb = 1 μg/kg; 1 ppm = 1000 ppb. Table 3 represents a summary of the commercially available SERS substrates (which is not exhaustive) and it is evident that each one of them have varied properties including the sensitivity, stability, and cost. Liu et al[130]. provided a comprehensive evaluation of six commercial substrates [Enspectrc-1 (Silicon based), Q-SERS™-1 (Silicon based), Ocean optics-3 (paper based Ag, Au; glass based Ag/Au) and Hamamatsu substrate-1 (Au NS on polypropylene)] including their sensitivity and reproducibility studies using the molecules of MB, BPE, 4-MBA. The SERS spectra recorded with XploRA-Plus Raman micro-spectrometer at 532 and 785 nm excitation wavelengths. From the results the authors observed optimized signals in the case of Enspectrc SERS substrate for all the three molecules at 532 nm; Q-SERS™ substrate for 4-MBA and BPE at 785 nm; Hamamatsu substrate for MB with 785 nm excitation. Hakonen et al[131]. have reported the SERS-based detection of forensic substances (Cyclosarin, RDX, Amphetamine and PA) using commercially available substrates and handheld Raman spectrometers. The same could be extended to flexible substrates provided they are efficient (providing high enhancements) for field applications. Further detailed research is required in this direction.

Conclusions and outlook

In recent years the development and applications of flexible SERS substrate has received incredible attention towards the detection of hazardous materials. In this review, we summarized the most recent research (focusing particularly on the last 3–4 years of research) on flexible based SERS substrates, including paper/cellulose, polymer nanofibers, 3D sponges, fabrics, etc., and their potential on-site detection of explosives, pesticides, chemical warfare agents, drugs for homeland security, food safety, and medical fields. There is a tremendous scope for the flexible SERS substrates in the above-mentioned fields and many others not listed here. Particularly in the field of explosive trace detection, these substrates will be

Table 3 | A summary of the commercially available SERS substrates, their costs, sensitivities and their stability (non-exhaustive).

S. No.	Company	SERS substrate	Sensitivity	Stability	Cost	Ref
1	**Stellarnet**	Cellulose with Au NPs	$\sim 10^6$	3 months	$199 (pack of 30)	ref.[186]
2	**Horiba France SAS**	Glass coated with Au nanorods processed by dynamic oblique vacuum evaporation	–	–	–	ref.[187]
3	**SERSitive**	Electrodeposition of silver and gold nanoparticles on an ITO glass surface	$\sim 10^5$–10^6	4 months	5 pcs Ag- €115 5 pcs Ag-Au- €138	ref.[188]
4	**EnSpectr Inc.**	Si/Glass passivated with a thin transparent dielectic layer.	$\sim 10^6$	Stable when unpacked	–	ref.[189]
5	**Silmeco**	Nanostructured Si deposited with Gold (Au), Silver (Ag)	–	–	5 units €350	ref.[190]
6	**Hamamatsu**	Au NS on polypropylene	–	3 months when unpacked	–	ref.[191]
7	**Integrated Optics**	Ag/Au coating on silicate glass.	–	2 months	Ag- €15 Au- €18	ref.[192]
8	**Mesophotonics. Ltd. Klarite**	Si	–	–	100 USD for single 2 mm × 2 mm sample.	ref.[193]
9	**Q SERS ™**	Au NSs on Si (5 mm × 5 mm)	ppb to ppm	6 months (package) 2 weeks (package opened)	2 units **$50 USD**	ref.[194]
10	**Metrohm**	Ag, Au based Filter paper	–	–	–	ref.[195]

highly beneficial. For example, explosives trace swiping/swabbing from luggage surfaces, clothing, vehicle surfaces, post-blast sites will be easier with such flexible substrates. These explosive molecules are sticky and leave behind small traces while handling and transporting them (on various surfaces). Such traces can be easily detected using efficient SERS substrates. Combined with a portable or handheld Raman spectrometers enriched with database/libraries of all explosive molecules, it presents a very attractive methodology for identification and prevention of terrorist activities. Similarly, testing food materials with these substrates enables prevention of easy adulteration (e.g., drinking water, milk, edible oils). Although there are several issues (e.g., further improvements in the sensitivity, long-term stability, reducing the costs) that need to be addressed for each of these methods. But there is also a huge scope for research in these areas, and we firmly believe the developments in these research areas will lead to practical devices.

Additionally, the recent developments in the understanding of SERS substrates (both plasmonic and non-plasmonic) and their potential have increased by leaps and bounds, the proof of which is evident from the number of review articles published in this area[196−198].

Different real-world applications that can be envisaged with these SERS substrates include

(a) Biomedical applications, bioimaging and biosensing[54,199,200];

(b) Inspection in food quality and safety[201];

(c) Biochemical and medical analysis[198];

(d) Virus detection (including COVID-19)[202,203];

(e) Plant disease diagnostics[204];

(f) Forensics[205].

Since there are numerous methods by which SERS substrates can be fabricated[206,207], it is imperative that a huge number of efforts are out to identify the niche application(s) for each one of them. For example, one may need to compromise on the cost if we need detection of femtomolar concentration of desired analyte molecule. Similarly, sensitivity is not an issue in some specific cases and cost needs to be considered. There are also tremendous advances in the preparation of nanofibrous mats[208,209] and combination of potential SERS NPs/NSs incorporation in these mats can lead to development of agile, low-cost, and versatile SERS substrates for various applications.

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Author contributions

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Competing interests

The authors declare no competing financial interests.