Metal nanoparticles/carbon dots nanocomposites for SERS devices: trends and perspectives

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Abstract

Carbon dots and carbon dots-based nanocomposites have found a myriad of technological applications. Despite the primary use of carbon dots as catalysts in the reduction process to form metal nanoparticles, their strong interaction with metal nanostructures in nanocomposites can be further exploited. By tuning the emission of carbon dots and the absorption band of metal nanoparticles, it is possible to reach adequate surface-enhanced Raman scattering (SERS) from the resulting nanocomposites. Herein, it is reported the state-of-art in metal/carbon dots nanocomposites applied as active elements for SERS devices in the detection of traces of analytes. Strategies of synthesis, morphology (aggregation and anti-aggregation methods) and the improvement in the homogeneous distribution of noble metal nanoparticles on substrates have been discussed to reach the best performance for highly efficient SERS devices.

Keywords Carbon dots · Graphene · Plasmons · Excitons · SERS · Ultra-trace detection · Raman spectroscopy

1 Introduction

Carbon dots are fluorescent zero-dimensional carbon-based materials with a diameter less than 20 nm, composed of centric carbon core (sp^2/sp^3 skeleton) of graphitic lattice or amorphous carbon form and functional groups-rich surface (carbonyl, hydroxyl, and amine), that gives rise to their excellent water solubility [1–4]. In general, synthetic methods for the production of carbon dots are classified in top-down or bottom-up methods. Top-down methods making use of raw materials as a carbon source and the graphite-derivatives (such as carbon nanotubes, graphene oxide, and so on), while the bottom-up are typically based on organic molecules [5]. In terms of classification, there are two important groups of carbon dots: graphene quantum dots (GQDs) and carbon nanodots (CDs). GQDs are composed of small fragments (single or few) of graphene sheets—carbon hexatomic ring honeycomb lamella (in groups of less than five layers) rich in

chemical groups at the edge (oxygen-containing function groups) that introduce effects of quantum confinement/edge effects [6]. The typical procedure for the production of GQDs is based on the oxidation-passivation of materials [7, 8]. Top-down based methods result in structures ranging from 3 to 30 nm, with circular or elliptical negatively-charged shape structures, rich in hydrophilic oxygen groups.

On the other hand, amorphous carbon forms are obtained from partial carbonization degree of carbon core with remaining chemical groups on the surface, and fluorescence originated from defects/surface states. The synthesis of CDs is established by the polymerization and more accessible method that explores the hydrothermal approach, ultrasonic and microwave-assisted methods [9], being the hydrothermal treatment the most common method in which a diversity of raw materials can be explored as a carbon source [5]. The typical geometry of CDs is spherical and the synthesis is environmentally

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avored in comparison with GQDs due to the absence of acid or strong oxidants in the overall process. The doping with N, P, S, and B atom and the abundant distribution of surface functional groups give rise the solubility in water and superior properties in terms of photoluminescence, tunable fluorescent, strong absorption, low toxicity, good biocompatibility, sensing (chemo- and bio-), anticounterfeiting, biomedicine, and catalysts [10], opening new possibilities for applications as SERS sensors. N-doped carbon dots with a diameter in the order of 9 nm (shown in Fig. 1—from Ref. [11]) are excellent supports for the green synthesis of silver nanoparticles for composites of N-dots/Ag NPs.

Surface-enhanced Raman Scattering (SERS) is a spectroscopic technique that makes use of the interaction of light with the surface of rough metal nanoparticles, making possible the chemical analysis of different analytes. The enhanced Raman signal from analyte (disposed on metal nanoparticles borders) is a consequence of high local electromagnetic field generated on specific sites of metal nanoparticles [12, 13] from the coupling of incident laser light and the localized surface plasmon resonance on the surface of metal nanoparticles (described as a primary source of electromagnetic enhancement) [14–19].

The overall process for enhancement in the Raman scattering is a result of two distinct mechanisms: the electromagnetic effect and the chemical effect [14–16]. The electromagnetic enhancement is a consequence of the excitation of localized surface plasmon from incident radiation with its frequency close to the plasmon characteristic oscillations. As a result, a resonance between excitation and the localized plasmon collective oscillations (perpendicular to the plane) takes place, enhancing the

resulting intensity by a factor of the order of E^4 . Metallic nanostructures of Cu, Ag, and Au are relevant prototypes for use in SERS devices due to the maximal enhancement at visible and near-infrared radiation.

In particular, the energy density of the incident electromagnetic radiation has been amplified around borders of plasmonic objects (noble metal surface) at the nanoscale—disposed at a critical distance to reinforce the near field. This process is also optimized at sharp edges, interparticle junctions and interface between nanoparticles. These regions with a high local field at nanoscale borders are so-called hot spots [20–22], that can also be formed at the interface between noble metal nanoparticles and metal substrates [23]. The second mechanism for SERS processes regards the chemical effect, which is based on inter- and intra-molecular charge transfer due to the electrons transference from the metal surface to the adsorbed species, reinforcing the resulting electric field [14, 15]. Based on these aspects, it is possible to observe that morphology, aggregation level and nature of metallic nanoparticles are critical parameters to reach adequate homogeneous dispersion of hot spots—as a consequence, the kinetics of the reduction process to form nanoparticles can be considered as a relevant step for the production of reproducible SERS templates for analyte traces identification.

Based on these aspects, it is worth mentioning that outstanding physical and chemical properties of carbon dots (such as chemical stability, low toxicity, and ease functionalization—surface modification) [24] have been conveniently explored for its use as a catalyst in metal nanoparticle synthesis. It is reported in the literature that N-doped graphene carbon dots are responsible for reinforcement in the SERS sensitivity in metal/GQD nanocomposites [25, 26] and that nanocatalyst concentration results in a higher concentration of metal nanoparticles [27]. It is also known that nitrogen-doped nanostructures (also rich in oxygen-based functional groups) favor the rapid conversion of silver nitrate to form silver nanoparticles [28]. This process has been considered for the synthesis of silver nanoparticles [29] and gold nanoparticles [30] by the action of trisodium citrate [27].

A different combination of chemical compounds (such as graphene oxide nanoribbons, graphene oxide, Na-doped carbon quantum dots, and N-doped carbon quantum dots) has been considered as catalysts for nanoparticles synthesis [30]. The adequate interaction of carbon dots and metal nanoparticles in composites takes place from an efficient coupling between plasmons from metal nanoparticle-surface and excitons from carbon dots [31, 32] which can also act as electron donors or acceptors to species incorporated into composites. This process is defined as surface plasmon-enhanced energy

Fig. 1 TEM images of N-doped carbon dots and the corresponding distribution of size. Reprinted with permission from Ref. [11]. Copyright (2016) American Chemical Society

transfer (SPEET) mechanism in which strong quenching is observed in the photoluminescence of carbon dots [33] associated with a blue shift in the emission of the composite. For this, strong coupling between the plasmons in the metallic nanoparticles and the excitons in carbon dots is required from the overlap between the absorption band of metal nanoparticles and the emission of carbon dots. It has been pointed out that the production of broad-band absorption-based systems (such as observed for silver nanorods) [32] leads to a better coupling, which in turn depends on the morphology of the resulting metal nanoparticles. On the other hand, the presence of hot spots is favored by the rich distribution of nanoscale gaps as observed in nanoscale edges and on the tip of the nanoparticles [34] as observed for wire-shaped copper nanostructures in composites with carbon dots [30]. The inhomogeneous distribution of hot spots generates a poorly reproducible SERS signal [35]. The general scheme

for a SERS assay is drawn in Fig. 2a that is a process favored by the abundance of hot spots (as graphically illustrated). A typical example of a SERS enhanced signal for analyte detection is shown in Fig. 2b (from Ref. [36]).

Different strategies have been applied to reach the required good SERS signal, such as the use of molecular probes. With this aim, it is reported the association of victoria B dye with gold nanoparticles [29] and rhodamine 6G associated with Cd@Ag nanocomposites applied in the detection of atrazine [37]—in this application, the analyte induces aggregation of silver nanoparticle-based composites. The change in the spatial distribution of metallic nanostructures (aggregation or anti-aggregation processes) introduces variation in the measured signal from the reporter molecule leading to increasing sensitive identification degree of different analytes [37]. More elaborated structures for SERS detection have been explored by the synthesis of core-shell assemblies of heteroatom

Fig. 2 **a** Experimental setup for SERS detection of specific analyte and the configuration of a typical hot spot formed by two nanoparticles. **b** Experimental results comparing the SERS signal from rhodamine 6G (Rh6G) at 4.2 mM (black trace), Rh6G/Au NP at 0.38 μM (red trace) and Rh6G/Au@CD NP at 0.38 μM (green trace). The left

figure shows TEM images of the nanostructures. It is noticeable the 10^4 times reduction in concentration, with a better signal to noise ratio for the Rh6G/Au@CD nanostructure. (**b** reproduced from Ref. [36], with permission from Royal Society of Chemistry)

systems of silver nanoparticles, SiO₂ and carbon dots [38], in which the distance between carbon dots and silver nanoparticles can be explored as a tuning parameter for optimization in the SERS signal. TEM images in Fig. 3 from Ref. [38] reveal the effect of a varying layer of SiO₂ for the final composite Ag@CD.

To evaluate the most adequate strategy to improve the SERS signal for identification of specific analytes, this review is organized as follows: in the following section, the procedure for nanocomposites preparation is presented in detail. In Sect. 3, it is summarized the procedure involved in the SERS support preparation, while in Sect. 4 it is described the performance in the detection of analytes and perspectives for future applications.

2 Preparation of composites

2.1 Synthesis of carbon-based nanostructures

The use of undoped carbon dots has been considered as the usual methodology for the production of SERS templates since 2012 [39]. More recently, the most relevant role of carbon dots has been focused on their function as strong catalysts to enhance the SERS activity of resulting composites [40]. The standard procedure reported in the literature refers to the production of carbon dots (undoped and N-, B-, S- and P-doped species) and applied as catalysts for the production of noble metal nanostructures. An example of this process refers to the incorporation of carbon dots into elastomer base together with reducing agent and silver nitrate, as reported in Ref. [31]. The standard methods applied in the production of carbon dots are described as follows:

The large scale production of carbon dots is typically based on precursors such as the biomass [41]. For this

Fig. 3 TEM images of Ag/PATP@SiO₂ nanoparticles with a silica shell thickness of **a** 0 nm, **b** 6 nm, **c** 9 nm, **d** 20 nm, **e** 35 nm and **f** composite with carbon dot. Reprinted with permission from Ref. [38]. Copyright (2016) American Chemical Society

condition, hydrothermal treatment is the most common method for the massive production of carbon dots [42, 43]. Moreover, the improvement in the optical properties of carbon dots has been reached from adequate doping with heteroatoms and by the introduction of amine passivants, making possible the modification of intrinsic properties such as the bandgap of materials. The hydrothermal treatment with carbon sources and heteroatoms substances (such as B, N, S and P) [44] make it possible to produce B-doped carbon dots (from reaction with boric acid) [45–47], phosphorous doped carbon quantum dots [48, 49] and S-doped structures [50, 51]. In terms of new methodologies for the production of N-doped carbon dots, the one-pot microwave-assisted method represents a cost-effective and ease-of-implementation method that makes use of nitrogen-rich precursors (such as L-Asparagine) [52]. The combination of raw materials as carbon source and nitrogen-rich materials represents an alternative to this process. The use of microwave-assisted processes from the association of citric acid (carbon source) and urea (nitrogen source) results in rich N-doped carbon dots [53]. Alternatively, graphene nanoribbons are produced using multiwalled carbon nanotubes as a precursor by corresponding hydrothermal assays, in a reaction with KMnO_4 and the following removal of byproducts (MnO_2) [30].

The doping level of resulting CDs/GQDs can be established from different routes. For instance, a simple procedure has been developed through the change of solvents applied in the hydrothermal procedure. Das et al. [25] reported the production of N doped graphene quantum dots (GQDs) from hydrothermal treatment in dispersions of graphene oxide in dimethylformamide, while S-doped GQDs are observed after hydrothermal treatment of dispersion of GO in dimethyl sulfoxide.

Other possibilities to produce N-doped carbon dots [54] are based on microwave-assisted methods in which a mixture of glucose is mixed with ammonium sulfite as a source of nitrogen for the production of N-doped carbon dots [27].

2.2 Synthesis of composites carbon dots/metal nanostructures

The standard method applied in the production of metal nanoparticles is based on the action of a reducing agent on the salt of metal ions, as schematically represented for reduction of silver from the action of sodium citrate (see Eq. 1)

The incorporation of carbon nanostructures (GQDs or CDs) in this process accelerates the redox electron transfer since their electron-rich structure favors the transfer of electrons, acting as reaction catalysts [55]. Different experimental systems have been reported for these ternary systems, such as from combination of graphene oxide/sodium citrate/ HAuCl_4 [30], GQD/ AgNO_3 /ascorbic acid [34], CD/ $\text{NaOH}/\text{AgNO}_3$ [24], N-dots/ $\text{NaOH}/\text{AgNO}_3$ [28] and $\text{NaBH}_4/\text{AgNO}_3/\text{CD}$ [56] for the following reaction that takes place in a water bath under controlled conditions. In general, the final nanocomposite is composed by metal nanoparticles decorated with carbon dots (see Fig. 4a [32] and b [56]) in which the synthesis of silver nanorods and the catalytic activity of graphene layers on the production of nanostructures are respectively explored.

Tang et al. [37] reported a modification in the standard method, making use of reporter molecules (rhodamine 6G) that are adsorbed on the surface of carbon dots that act as a reducing agent for reaction under controlled temperature in a water bath. As a result (see Fig. 4c) it is possible to reach a configuration in which carbon dots are decorated with silver nanoparticles and reporter molecules (rhodamine 6G). The aggregation induced by analytes affects the distribution of hot spots and strongly reduces the characteristic emission peak of the reporter molecule, allowing that low detection level of analytes can be reached.

A more elaborated assembly of nanoparticles is reported by Zhang and Du [38] that developed nanocomposites in which a covering layer of SiO_2 act as a spacer, separating the core (silver nanoparticle) and the carbon dots—this layer can be used as a tuning parameter applied in the optimization of energy transfer between silver surface plasmons and excitons from carbon dots—schematically drawn in Fig. 4d.

3 Preparation of SERS devices

One of the most important steps for analyte detection by SERS technique refers to the adequate production of SERS substrates. This process is critically important due to the required homogeneous distribution of plasmonic centers on supports to generate reproducibility for scattering pattern. With this aim, different strategies have been considered in the literature to produce SERS substrates, based on the production of simple devices, such as from the deposition of droplets containing nanoparticles on glass (or quartz slides) to more elaborated strategies, in which the reuse of devices is provided by simple washing procedure. The scheme is shown in Fig. 5 and summarizes the most common substrates explored for SERS detection assays, which varies from microfluidic devices until super-hydrophobic surfaces, described as follows.

Fig. 4 Different configuration of carbon dots/metal nanostructures-based nanocomposites: **a** silver nanorods decorated with carbon dots (Ag@CD structure); **b** silver nanoparticles coated by a thin

layer of graphene oxide; **c** CD@Ag (core-shell) nanoparticles/R6G; **d** silver NP@SiO₂ (core-shell) nanoparticles with a coating layer of SiO₂ decorated with carbon dots

Fig. 5 Description of different substrates explored as support for SERS signal detection

The simplest procedure to produce solid-state supports is the direct transfer of nanocomposites and analytes to the quartz cells for direct measurement of scattering patterns [27, 29, 38] and from the dispersion of droplets of

nanocomposites on quartz plates [37]. Alternatives are observed from the use of paper-based devices [27] with advantages related to the intrinsic porous structure of cellulosic fibers (such as the adsorption). Another possibility to produce SERS devices on natural fibers has been observed from the synthesis of metal nanoparticles on fibers of eggshell membranes [57].

The deposition of nanocomposites on Si substrates takes place from direct dip coating of nanocomposites on cleaned Si (100) substrates [25] and the self-assembly of structures upon electrostatic interaction on treated surfaces [56].

Another simple methodology to remove the liquid phase and to reach a solid film (in the scale of few micrometers) refers to the filtration of reactional media into specific membranes (with controlled porosity). The vacuum-assisted filtration accelerates the removal of the liquid phase maintaining the solid phase on the filter paper surface until to reach self-standing films after complete elimination of solvent. A standard procedure concerns the filtration of nanocomposites in PTFE membranes followed by drying of solid material for a posterior step in which

the film is peeled off to be applied as SERS substrate [34, 58]. Alternatively, Bhunia et al. reported the development of flexible supports of polydimethylsiloxane embedding carbon dots for the following step of coating with silver nanoparticles, as schematically drawn in Fig. 6 (from Ref. [31]).

The electrochemical deposition of silver on a 2D network of single-walled carbon nanotubes represents another important strategy to control the aggregation level of metal nanostructures [59]. In the same direction, the production of silver dendrites is electrochemically conducted on commercial aluminum foil and results in a material with a high area-to-volume ratio [60]. The self-assembly of silver nanostructures is described in Ref [61] in which silver nanoparticles are deposited on the tip of conventional optical fibers through a layer-by-layer procedure that explores the backscattering of light in the presence of analytes. Superhydrophobic structures are described in Ref. [62] which are based on the electrochemical growth of silver nanostructures on a gold seed layer.

In terms of promising strategies for more efficient templates for SERS, it is worthy to mention that lab-on-a-chip applications can be favored by integration with

SERS-based microfluidic networks. An example can be seen in Ref. [63], where SERS supports composed of Ag dendrite in T-type microfluidic devices are demonstrated.

Guo et al. reported the production of sub-microspheres of Au@MoS₂@Au that were flatted on the surface of the silicon wafer. The self-cleaning is provided by the photocatalytic process since the samples are illuminated for 30 min under visible light and get ready for the next round of detection after a simple washing procedure [64].

4 Performance in the detection of analytes

The development of highly efficient SERS templates depends on a complex combination of factors such as the nature of substrate, the plasmonic center (type and distribution), the prevailing energy transfer process in

heterostructures-based devices, the formation of multiple hot spots at interfaces of substrate/nanostructures (and in the gap of nanostructures) and the disposition of analyte into the nanoparticles array [65].

In particular, the detection of single molecules introduces a typical drawback related to the lack of reproducibility patterns at the nanoscale. As a consequence, it is required a well-defined pattern of nanostructures on substrates to reach desirable values for the Raman enhancement factor (EF). Jiwei et al. [66] explored periodic arrays of metal nanopillars with gap size in the order of 10 nm and observed EF in order of 2×10^8 . In addition to the regular distribution of nanostructures, another important strategy refers to the improvement in the stability of the overall device. The use of film chips based on polyethylene terephthalate as support for plasmonic structures results in values for EF in order of 3.14×10^6 [67].

However, the performance of carbon dot-based SERS devices is still hindered by the low EF values (as a consequence of wavelength-dependent emission behavior) [68]. The typical values for nitrogen-doped graphene quantum dots are reported to be in the order of 3.2×10^3 [25].

To circumvent these limitations, heteroatom-based structures have been considered a promising strategy to reach superior performance in terms of EF value. Based on this strategy, it is reported values of 10^7 for N-doped carbon dots—Au@AgNPs core-shell structures [69], while enhancement factor in order of 10^8 is observed for branched silver—supported carbon dots [32] and EF values in order of 10^6 – 10^7 for systems composed by free-standing Si nanowires decorated with Au/graphene nanoparticles that favor the creation of “multiple hot spots” [70]. These results confirm that improved SERS response for carbon dots-based systems depends on the combination of electromagnetic and chemical mechanisms [70] that can be explored from noble metal arrays, porous substrates and by the interaction of these structures with substrates, allowing the formation of hot spots at different scales and levels.

Fig. 6 Scheme of preparation of C-dot-Ag-NP-PDMS films (carbon dots represented by yellow dots and silver nanoparticles as red dots on flexible support of PDMS). Reprinted with permission from Ref. [31]. Copyright (2016) American Chemical Society

Another relevant parameter to evaluate the performance of SERS devices refers to the measurement of the limit of detection for specific analytes, as an indication about the potential of an experimental system to reach the ultra-trace limit for identification of contaminants. Table 1 summarizes the limit-of-detection for different experimental SERS systems applied in the identification of specific analytes.

As can be seen, the limit of detection for different analytes is in a broad range of μM –fM. By comparison of different experimental systems with the same analyte (if considered the rhodamine B, rhodamine 6G and p-aminothiophenol) it is possible to observe that limit of detection of rhodamine 6G varies from 10^{-6} to 10^{-15} M for different SERS devices while the corresponding variation for rhodamine B is in the range of 10^{-10} to 10^{-14} M and the limit of detection of p-aminothiophenol is in the range of 10^{-8} to 10^{-9} M. It is important to observe from these data that low performance in terms of LOD is observed for systems based on pure metal nanoparticles (as an example, for detection of rhodamine 6G) are limited to values in order of 10^{-6} – 10^{-7} M. On the other hand, if considered heteroatom-based systems (composed of two or three components), the LOD for rhodamine 6G is in the range of 10^{-10} – 10^{-15} M. The same behavior is observed in the LOD value for rhodamine B—the value observed for pure carbon derivative is improved by

association with nanoparticles in a synergistic process that improves the performance of the overall device.

As previously observed, the good performance observed for heteroatoms –based SERS systems is a consequence of a higher density of hot spots, created not only by gaps between noble metal nanoparticles but also from the interaction of components and roughness degree of support. The adequate combination of electromagnetic and chemical mechanisms as a source of effective SERS signal can be reached from the adequate energy transfer process from carbon dots to noble metal nanoarrays. These results confirm the relevance and promising possibilities for SERS devices based on the hybrid configuration of noble metal structures modified by carbon dots incorporation.

5 Conclusions and outlook

The development of highly efficient SERS devices depends on the adequate coupling of carbon dots and metallic nanoparticles (in terms of energy transfer between parts), adequate morphology (creation of hot spots), and homogeneous dispersion of hot spots in active SERS templates. The association of carbon nanodots and graphene quantum dots as catalysts for metal nanoparticle production results in nanocomposites with high performance for the detection of traces of analytes. The use of flexible and porous

Table 1 Comparison of the limit of detection for different analytes

Material	Analyte	Detection limit	References
N-GQD/Rhodamine B	Rhodamine B	10^{-10} M	[25]
Carbon nitride QDs/Ag NPs into graphene layers		10^{-14} M	[34]
Ternary flexible membranes of reduced GO with Ad meso-flowers and carbon nitride nanosheets	Rhodamine 6G	10^{-15} M	[58]
Ag rods-supported carbon dots		10^{-10} M	[32]
Nanoparticles-modified optical fiber tip		2×10^{-7} M	[61]
Au nanoparticles substrates		10^{-6} M	[71]
N-CD/Ag NPs	Biotin	0.3 pg/mL	[27]
Graphene oxide nanoribbon/gold nanoparticles	Glucose	0.13 nM	[30]
Carbon nitride QDs/ Ag NPS into graphene layers	Methylene Blue	10^{-14} M	[34]
Silver nanoparticles—carbon dots core–shell	Uric acid	0.01 μM	[24]
CD@Ag—rhodamine 6G -atrazine	Atrazine	0.01 μM	[37]
Ag-doped carbon dots nanogold particles	Pb (II)	0.006 μM	[26]
Ca-doped carbon dots for reduction of gold nanoparticles	Thrombin	0.0058 nM	[29]
Gold nanoparticles on a paper strip	Mucin-1	500 ng/mL	[35]
Ag NPs/N-dots nanocomposites	Malachite green	2.7 nM	[28]
	Crystal violet	2.0 mM	
Silver nanoparticles/carbon dots	p-aminothiophenol	10^{-9} M	[72]
Ag@CDs nanocomposites		10^{-8} M	[33]
Ag@SiO ₂ decorated carbon nanodots	Goat-anti-mouse IgG	0.01 $\mu\text{g/mL}$	[38]
Carbon-based dot capped silver nanoparticles	4-Aminothiophenol	5×10^{-11} M	[56]

membranes represents an important strategy to produce supports with a homogeneous distribution of hot spots to improve the limit of detection. Based on these properties and associating the action of nanoparticles, it is possible to reach detection as low as 10^{-15} M.

The maturing of environmentally friendly and green chemistry-based substrates for SERS detection has been successfully motivated by the production of multiple-use substrates and self-cleaning SERS-based devices. The results reported in this review demonstrated superior performance for ternary systems based on reduced graphene oxide as a supporting layer for silver meso-flowers and phenyl modified graphitic carbon nitride nanosheets that explored the photocatalytic-driven procedure to reach self-cleaning requirements. Also, the better performance for the detection of rhodamine 6G is a consequence of strong hot spots structure due to the intraparticle interaction. On the other hand, good performance has been described for graphene quantum dots applied as catalysts for silver nanoparticles reduction. However, scarce attention has been dedicated to the development of “all-graphene” devices. These multifunctional assemblies can be explored not only as SERS templates but also as a catalyst for the production of metal nanoparticles and mesostructures.

Therefore, the perspective of the production of flexible, reusable and green-based SERS devices for ultra-trace detection of analytes represents an important frontier to be achieved. Further potential interfacing materials are layered transition metal dichalcogenides (LTMDs), as already pointed out by Vallan et al. [73] or LTMDs-based QD, which can be synthesized by laser ablation [74].

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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