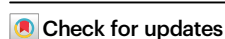


Low curvature combined with high amorphization improves SERS sensitivity of semiconducting Rh–Se mesoporous nanospheres toward non-adsorbing resistant pollutants

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Amorphous metal–selenium (M–Se) alloys hold promise for applications such as catalysis, electronics, and surface-enhanced Raman spectroscopy (SERS) sensing due to their surface reactivity, isotropic properties, and tunable bandgap. However, controlling the synthesis of nanostructured noble-metal-based M–Se materials is difficult, as the strong metallic bonding and low chemical reactivity of noble metals hinder homogeneous selenization. Here we show a one-step micellar self-assembly reduction method to produce amorphous semiconducting Rh–Se mesoporous nanospheres (a-Rh–Se MNs). We systematically investigate how composition, surface curvature, and crystallinity affect SERS performance. a-Rh–Se MNs with low curvature and high amorphization achieve enhanced sensitivity toward typically non-adsorbing, low-polarizability analytes, including hexachlorobenzene, anthracene, and polytetrafluoroethylene microplastics (even in wastewater). Combined experimental and theoretical analyses reveal that co-modulating curvature and amorphization tunes key electronic descriptors (e.g., d -band center and work function), thereby promoting resonant charge transfer. This finding overturns the conventional paradigm that prioritizes high-surface-area substrates. Our work establishes mesostructured a-Rh–Se for SERS applications and provides insights into M–Se surface chemistry for designing advanced SERS materials.

Amorphous materials offer distinct advantages, including enhanced surface reactivity, isotropic properties, and the absence of grain boundaries, which can be advantageous for applications in catalysis, sensing, and electronics^{1–3}, although their intrinsic structural disorder may also introduce defect states and reduced charge carrier mobility. Conventional routes to amorphous phases, such as quenching rapidly from the molten state, are well established⁴.

However, these methods face limitations when applied to close-packed noble metals like Ag, Au, Ir, Pt, and Rh due to their inherent propensity for rapid crystallization⁵. Although incorporating non-metallic (e.g., P, Se) or metalloid elements (e.g., B, Te) via wet-chemical reduction effectively suppresses crystallization and promotes amorphous alloy formation^{6–8}, precise atomic-level control of amorphous nanostructures remains a challenge.

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Metal–selenium (M–Se) amorphous alloys (e.g., Rh–Se, Pt–Se) have emerged as a compelling class of metal chalcogenide semiconducting materials exhibiting advantageous properties^{9–13}. Metal chalcogenides have shown promising performance in areas such as the electrocatalytic nitrogen-reduction reaction¹⁴ and surface-enhanced Raman scattering (SERS)^{15,16}. Despite their potential, several challenges hinder the rational design and application of amorphous M–Se materials. First, the intrinsic long-range atomic disorder of amorphous structures makes precise control over nanoscale morphology difficult⁵. Amorphous metal selenides are typically obtained in the form of nanoparticles^{14,17}, rather than in well-defined architectures, such as mesoporous structures, which are particularly attractive due to their tunable porosity and broad application potential¹⁸. Second, the formation of amorphous phases is highly sensitive to composition¹⁹, yet the relationship between the M/Se ratio and phase evolution remains poorly understood. Third, a systematic understanding of how different degrees of crystallinity influence structural and chemical functional properties is still lacking. Fourth, the surface and interface chemistry of amorphous M–Se materials remains insufficiently controlled. These knowledge gaps limit advances in the controlled synthesis and structure–property correlation of amorphous materials.

Recently, the deliberate manipulation of nanoscale curvature has emerged as a strategy for tailoring material properties^{20–23}. Such geometry-dependent effects have also been observed in related nanostructured systems, where size or curvature influences surface chemistry and interfacial behavior²⁴. For example, nanostructures with smaller surface curvature radii resulted in higher-concentration ion distributions for enhanced capacitive deionization performance²⁰. Chen et al.²¹ reported that the curvature engineering of Pt nanocones can greatly promote the H_3O^+ supply rate during electrocatalytic hydrogen evolution reaction. In the context of SERS, manipulating curvature alters the interaction between adsorbates and the semiconductor surface in many different aspects (surface area, specific adsorption sites, electronic structure, band alignment, etc.), thereby influencing chemical enhancement²⁵. Inspired by these insights, we hypothesize that integrating amorphization with curvature modulation in Rh–Se mesoporous nanostructures offers an effective platform for tuning semiconductor SERS activity. This dual approach may enable detection beyond model analytes, such as dyes or thiols, but the detection of non-adsorbing and low-polarizable analytes remains a long-term challenge, limiting semiconductor applications in SERS. The commonly used semiconductors, such as Cu_2O ²⁶, ZnO ²⁷, TiO_2 ²⁸, MoTe_2 ²⁹, ZnSe ³⁰, and CdSe ³¹, show limited adsorption toward non-adsorbing and low-polarizable analytes, leading to poor electronic coupling³².

Here, we present a facile, one-step synthesis of amorphous Rh–Se mesoporous nanospheres (a-Rh–Se MNs) with tunable curvature via micellar self-assembly chemical reduction. We systematically investigate the influence of composition and thermal treatment temperature on the resulting crystallinity and, critically, on their performance in SERS. We find that a-Rh–Se MNs with lower surface curvature and reduced surface area exhibit SERS activity, contrary to the intuitive and commonly observed high SERS sensitivity of high surface area materials. Unlike the commonly reported SERS sensing of highly polarizable molecules—which readily adsorb onto and interact with the substrate—we focused on the more challenging detection of low-polarizability, surface-resistant pollutants. The lowest limit of detection (LOD) for hexachlorobenzene (HCB) and polytetrafluoroethylene (PTFE) microplastics (MPs) was achieved with low curvature and highly amorphous a-Rh–Se MNs. We attribute this performance to the synergy between the amorphous structure (providing optimum electronic features and abundant active sites) and nanoscale curvature modulation (tuning surface energy levels, thereby improving electronic coupling and orbital alignment with the analyte). This work provides deeper insights into the synthetic chemistry of amorphous nanomaterials and

significantly advances the understanding of the structure–property relationships in these complex systems. Our results challenge conventional SERS design paradigms and offer insight into semiconductor–analyte interactions critical for real-world pollutant sensing.

Results

Synthesis of a-Rh–Se MNs with various compositions

The amphiphilic poly(ethylene oxide)-*b*-poly(methyl methacrylate) (PEO-*b*-PMMA) diblock copolymer served as a dynamic soft template to engineer tunable compositions and mesoporosity in a-Rh–Se MNs via a one-pot micelle-mediated reduction (Fig. 1a). Upon introducing Rh/Se precursors ($\text{Na}_3\text{RhCl}_6/\text{H}_2\text{SeO}_3$) and water into the tetrahydrofuran (THF)-polymer solution (see Methods), PEO coronas selectively sequestered metal ions around PMMA cores, initiating uniform micelle nucleation (validated by the Tyndall effect in Supplementary Fig. 1 and Supplementary Movie 1). Subsequently, the solution was left at 80 °C for 12 h, during which formic-acid-driven reduction and Rh–Se coalescence occurred within the micellar scaffold. Subsequent template removal unveils an interconnected porous framework of typical a-Rh–Se MNs with relatively large mesopores (a-Rh–Se-L MNs), as observed in scanning electron microscopy (SEM) images (Supplementary Fig. 2), bright-field transmission electron microscopy (TEM) image (Fig. 1b, c and Supplementary Fig. 3a), and scanning transmission electron microscopy (STEM) images (Fig. 1d Supplementary Fig. 3b, c). The network of mesopores is absent in the nonporous control sample (i.e., a-Rh–Se-np, Supplementary Fig. 4).

The composition ratio of a-Rh–Se MNs can be precisely tuned by controlling the Rh/Se precursor ratio (see “Methods”), with the final alloy composition following the same trend as the precursor feed ratio, as confirmed by inductively coupled plasma optical emission spectrometry (ICP-OES) and SEM energy-dispersive X-ray spectroscopy (EDS) (Supplementary Table 1 and Supplementary Figs. 5–8). Powder X-ray diffraction (XRD) analysis was employed to probe the correlation between crystalline structure and Rh/Se stoichiometry. We observed that as the Rh content in Rh–Se alloys increased, the mesostructure remained (see SEM images in Supplementary Figs. 6 and 7); however, at a critical Rh composition of ≈ 67.8 at.% (i.e., feeding molar ratio of Rh/Se = 3:1), the face-centered cubic (fcc) Rh crystalline phase became predominant (Fig. 1e). Conversely, progressive reduction in the Rh ratio (i.e., increased Se content) led to a gradual predominance of amorphous character. This inverse relationship implies that Se acts as a pivotal amorphous-phase inducer in these alloy systems. We probed different Rh_xSe_y compositions towards HCB sensing via Raman spectroscopy with 532 nm excitation wavelength. HCB (10^{-6} M) was chosen as a probe molecule, and the peak at 375 cm^{-1} (C–Cl stretching vibration) was used as a characteristic for the enhancement factor (EF) analysis because this mode provides a strong and spectrally isolated signal with minimal overlap from substrate or background contributions, enabling reliable quantitative comparison across samples. We found that a-Rh–Se-L MNs with a feeding molar ratio of Rh/Se = 1:3 provide the highest $\text{EF} > 4 \times 10^3$, and a further increase of Rh percentage does not lead to an increase of EF (Supplementary Fig. 9). Therefore, further studies focused on a-Rh–Se-L MNs with a final Rh:Se atomic ratio of 20:80 (obtained by ICP-OES, Supplementary Table 1).

The amorphous nature of the typical a-Rh–Se-L MNs was also carefully studied by using characterization techniques of high-resolution TEM (HRTEM) and selected-area electron diffraction (SAED). The absence of distinct lattice fringes in the HRTEM image (Fig. 1c) and the broad diffraction rings in the SAED pattern (inset of Fig. 1c) collectively confirmed the amorphous nature of the a-Rh–Se-L MNs, as also evidenced by diffuse fast Fourier transform (FFT) rings (Supplementary Fig. 10). STEM-EDS maps show a uniform distribution of Rh and Se throughout a single MN (Fig. 1d and Supplementary Fig. 11).

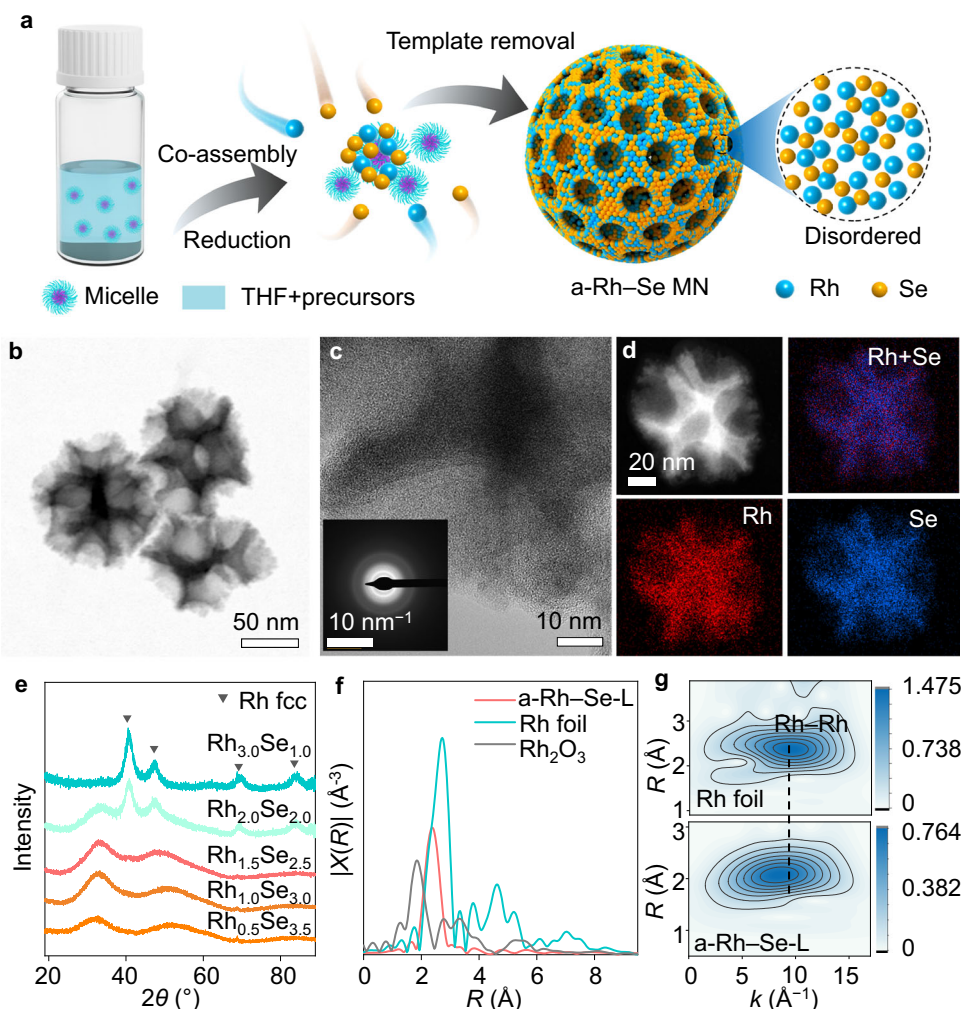


Fig. 1 | Schematic of material synthesis and characterization of a-Rh-Se-L mesoporous nanospheres (MNs). **a** Illustration of the synthesis route of micelle-induced wet-chemical reduction synthesis of a-Rh-Se MNs. The dark regions in a-Rh-Se MN represent surface voids, corresponding to pore sites in the mesoporous Rh-Se framework. **b** Bright-field TEM, **c** HRTEM, **d** HAADF-STEM and corresponding EDS mappings of a-Rh-Se-L MNs. The inset of **(c)** shows the SAED pattern from a single a-Rh-Se-L MN. The experiment in **(b–d)** was independently repeated three

times with similar results; representative results are shown. **e** Powder XRD patterns of a-Rh-Se with various compositions (fcc: face-centered cubic). **f** Fourier transform extended X-ray absorption fine structure of a-Rh-Se-L MNs with standard references. **g** EXAFS wavelet-transform spectra of Rh foil (top) and Rh-Se-L MNs (bottom) providing a high resolution in both k and R spaces. Source data are provided as a [Source data](#) file.

To investigate the chemical states and local coordination environments of Rh and Se in the a-Rh-Se-L MNs, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine-structure (EXAFS) measurements were carried out at both the Rh and Se K -edges. Metallic Rh foil and Rh_2O_3 were used as references for Rh, while Se foil and SeO_2 served as references for Se. Analysis of the Rh K -edge XANES spectra revealed that the first-derivative maximum for the a-Rh-Se-L MNs appeared at ≈ 23222.6 eV (Supplementary Fig. 12a), positioned between that of Rh foil (23219.3 eV) and Rh_2O_3 (23226.4 eV). Based on a linear correlation between oxidation state and the edge position (Supplementary Fig. 12b), the average valence of Rh in the a-Rh-Se-L MNs was estimated to be $\approx +1.4$ (estimated from the calibration). The small amount of the oxidized species may originate from partial oxidation upon exposure to air. In the Se XANES spectrum (Supplementary Fig. 13), the Se in Rh-Se is mainly present in a near-zero oxidation state, similar to that of the Se reference, rather than SeO_2 . The surface chemical state of a-Rh-Se-L MNs was also probed by X-ray photoelectron spectroscopy (XPS) (Supplementary Fig. 14). The results indicate that surface Rh exists in a coexistence of metallic and oxidized states, while Se is primarily present in its zerovalent state.

The EXAFS analysis at the Rh K -edge of a-Rh-Se-L MNs (Fig. 1f) reveals a local structure in Rh-Se, characterized by a dominant coordination peak at ≈ 2.38 Å, which could be assigned to Rh-Se bonding, matching well with other reported metal-Se compounds³³. This contrasts sharply with reference Rh foil and Rh_2O_3 spectra, where distinct Rh-Rh (≈ 2.73 Å) and Rh-O (≈ 1.84 Å) scattering paths typically appear at longer and shorter distances, respectively. To elucidate the local coordination environment and atomic distribution of Rh in a-Rh-Se-L MNs, wavelet-transform analysis of k^3 -weighted EXAFS spectra revealed a dominant Rh-Se bonding feature in contrast to the characteristic Rh-Rh metallic bonding observed in Rh foil (Fig. 1g).

Curvature modulation of a-Rh-Se MNs

Surface curvature was tuned by adjusting the pore size. During chemical reduction synthesis, PEO-*b*-PMMA served as both surfactant and pore-forming template, with the PMMA molecular weight dictating pore diameter—higher PMMA molecular weights produced larger pores, as confirmed by SEM (Supplementary Fig. 15), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and STEM tomography renderings (Fig. 2a–c, Supplementary Figs. 3, 11, and 16). The amorphous structures of

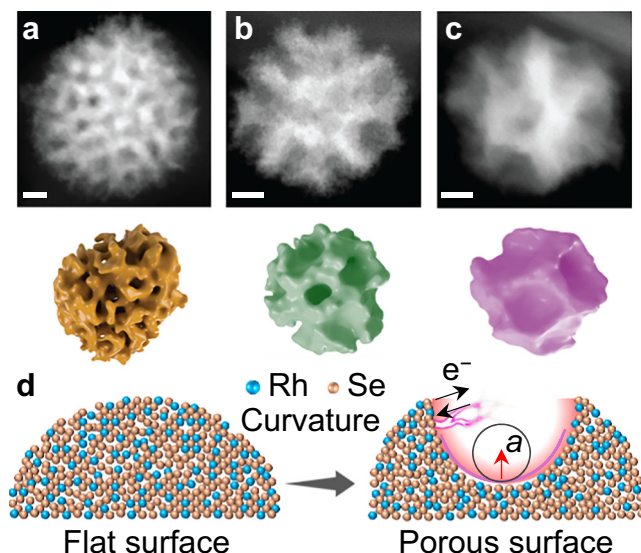


Fig. 2 | Structural characterization with different curvatures. HAADF-STEM images and STEM tomography renderings of **a** a-Rh-Se-S (yellow), **b** a-Rh-Se-M (green), and **c** a-Rh-Se-L (purple). Scale bars: 20 nm. The experiments in (a–c) were independently repeated three times with similar results; representative results are shown. **d** The schematic illustration of curvature variations in porous surface with enhanced charge transfer.

a-Rh-Se-S (S: small pore of ≈ 8 nm), a-Rh-Se-M (M: middle pore of ≈ 20 nm), and a-Rh-Se-L (L: large pore of ≈ 26 nm) were confirmed by XRD patterns (Supplementary Fig. 17). Samples a-Rh-Se-S and a-Rh-Se-M exhibit surface chemical states similar to those of sample a-Rh-Se-L (Supplementary Fig. 14). The high-resolution O 1s and C 1s analyses further indicate that the Raman enhancement is not dependent on uncontrolled C/O contributions. Small-angle X-ray scattering (SAXS) measurements indicate the presence of a uniformly distributed porous structure within the porous a-Rh-Se ensemble (Supplementary Fig. 18). Among them, the Brunauer–Emmett–Teller specific surface area obtained by N_2 adsorption–desorption measurements follows the order: a-Rh-Se-S ($41.1 \text{ m}^2 \text{ g}^{-1}$) > a-Rh-Se-M ($37.2 \text{ m}^2 \text{ g}^{-1}$) > a-Rh-Se-L ($29.1 \text{ m}^2 \text{ g}^{-1}$). However, subsequent SERS measurements (further discussed later) revealed that the a-Rh-Se-L MNs delivered stronger enhancement than a-Rh-Se-S MNs and a-Rh-Se-M MNs (the sample with middle pore size), indicating that SERS activity does not correlate directly with specific surface area (Supplementary Fig. 19).

Here, we therefore proposed a conceptual concave porous structure to investigate the effect of curvature engineering (Fig. 2d), where the Gaussian curvature is expressed in Eq. 1:

$$K = k_1 k_2 \quad (1)$$

where k_1 and k_2 are the principal curvatures at a given point, (representing the maximum and minimum curvature, respectively)³⁴. In this work, since the pore-forming agents (i.e., PEO-*b*-PMMA micelles) are spherical³⁵, the resulting mesopores are approximated as spherical structures for the convenience of quantitative analysis. In such a case, any point on the inner surface of a spherical pore has two equal principal curvatures. For a concave spherical surface, both principal curvatures are negative and equal to the inverse of the pore radius, Eq. 2:

$$k_1 = k_2 = -\frac{1}{a} \quad (2)$$

where a is the pore radius.

As a result, the Gaussian curvature was obtained by following Eq. 3:

$$K = k_1 k_2 = \left(-\frac{1}{a}\right) \left(-\frac{1}{a}\right) = \frac{1}{a^2} \quad (3)$$

For a-Rh-Se-S, -M, and -L with approximate pore diameters of 8, 20, and 26 nm, respectively, the corresponding K are 0.063, 0.010, and 0.0059 nm^{-2} . The curvature engineering induced changes in the surface structure. Valence-band XPS analysis revealed that the d -band center ε_d shifts progressively upward with decreasing curvature (curvature degree order: a-Rh-Se-S > M > L) (Supplementary Fig. 20). To ensure the reliability of these subtle electronic shifts, each measurement was repeated in triplicate; the resulting standard deviation for ε_d is less than 0.025 eV, which is well within the statistical confidence interval for trend analysis. This shift is a consequence of enhanced surface strain and reduced atomic coordination at smaller curvature, which modulates the d -electron distribution. Potential artifacts from surface charging or contamination were excluded by employing an electron flood gun and rigorous C 1s calibration (284.8 eV) across all samples. A related geometry-dependent effect has been reported in nanostructured systems²⁴. Concurrent atomic force microscope (AFM) measurements of the work function (Φ) showed the sequence a-Rh-Se-S (4.723 eV) > a-Rh-Se-M (4.713 eV) > a-Rh-Se-L (4.702 eV) (Supplementary Figs. 21 and 22), with the lowest Φ in a-Rh-Se-L facilitating more efficient electron emission and metal–molecule charge injection. Together, these findings indicate that as curvature decreases, the lower d -band center affects energy-level alignment for the chemical enhancement mechanism (CEM) of SERS, while the reduced Φ promotes electron transfer from the metal to the adsorbed molecules.

Crystallinity modulation of a-Rh-Se-L MNs

Considering the temperature sensitivity of amorphous materials, which tend to crystallize upon heating, this study systematically investigated the structural evolution of typical a-Rh-Se-L MNs through controlled thermal treatments under an inert atmosphere and their structure–activity relationship in SERS performance, as will be discussed subsequently. Figure 3a illustrates the schematic structural transformation scheme during annealing, along with the corresponding XRD patterns documenting the crystallization process (Supplementary Fig. 23). The thermally treated samples were designated as Rh-Se- x , where x denotes the annealing temperature (in $^\circ\text{C}$). The results demonstrate that the as-prepared a-Rh-Se-L MNs exhibit an amorphous structure, showing slight crystallization and a small increase in crystallite size (from 1.54 to 2.00 nm) after treatment at 200°C (i.e., Rh-Se-200 MNs) (Supplementary Table 2). However, annealing at 400°C induced crystallization, yielding crystallites with an average size of 7.27 nm at $2\theta = 32.9^\circ$, consistent with the RhSe_{2+x} phase (PDF#19-1047). Upon further heating to 600°C , the crystallite size of Rh-Se-600 MNs increased substantially to 15.3 nm, accompanied by distinct phase separation into a mixture of Rh_3Se_4 (PDF#19-1051) and fcc Rh (PDF#05-0685). This structural evolution indicates elemental rearrangement within the Rh–Se system during thermal processing.

To further investigate this transformation, the samples were characterized using TEM, STEM, SAED, and HRTEM analysis. Post-annealing materials retained a well-defined mesoporous structure (Fig. 3b–d and Supplementary Fig. 24). Enhanced crystallinity was confirmed by SAED patterns, with HRTEM images providing corroborative evidence (Fig. 3b–d). The compositional analysis revealed a progressive decrease in the relative Se content and a corresponding increase in Rh concentration (Rh/Se = 21/79, 33/67, and 72/28 for Rh-Se-200, Rh-Se-400, and Rh-Se-600 MNs, respectively) within the Rh–Se MNs as the annealing temperature rose (Supplementary Fig. 25).

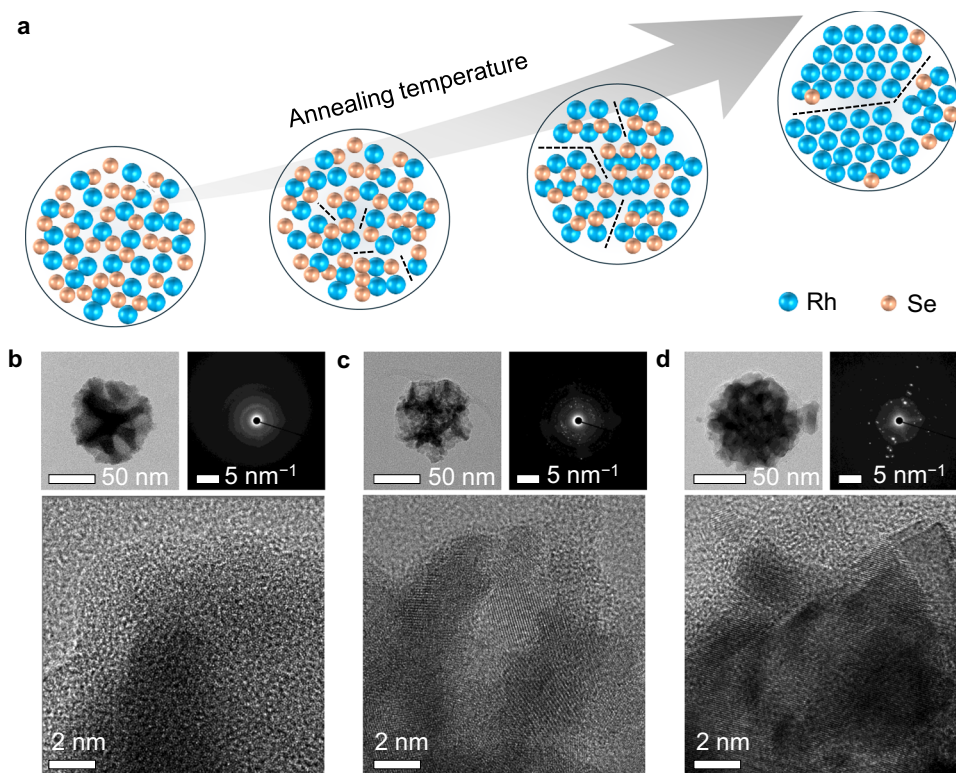


Fig. 3 | Preparation and characterization of Rh-Se MNs with different crystallinity. **a** Schematic diagram of the sample preparation with increasing annealing temperatures. TEM images, SAED patterns, and HRTEM images of **b** Rh-Se-200,

c Rh-Se-400, and **d** Rh-Se-600 MNs. The experiment in (b–d) was independently repeated three times with similar results; representative results are shown.

This process destabilizes the metastable coordination environment of Rh atoms previously bound to Se, consequently promoting the formation of Rh–Rh metallic bonds.

SERS performance of various Rh–Se samples

In this work, we aimed to sense resistant pollutants like chlorinated aromatics and polyfluorinated molecules that accumulate in the environment because of resistance to degradation^{36,37}. While semiconductor sensors can detect certain resistant gaseous pollutants, such as CH₄ and CF₄, via adsorption-induced changes in electrical conductivity³⁸, they lack the major advantages of SERS sensing, such as selective molecular fingerprint identification under ambient conditions. However, potential difficulty in their detection using semiconductor-based SERS arises from their resistance to adsorption and surface interactions, which prevents polarization or dipole generation³². This is because common semiconductors shaped in layered films or nanoparticles (NPs), such as Cu₂O, ZnO, TiO₂, MoTe₂, ZnSe, CdSe, have mainly been demonstrated using readily adsorbing model analytes, whereas the detection of weakly adsorbing analytes remains challenging^{39,40}. This is contrasting with the sensing of commonly reported model dye Rhodamine 6G, methylene blue (MB), and 4-mercaptopyridine on semiconductors, where analytes are easy to polarize. In addition to CEM, defect-induced localized charge accumulation in semiconductors can generate nano-localized electric fields under optical excitation, contributing to Raman enhancement even in non-plasmonic systems⁴¹. However, this pathway is not considered in detail within this study. We started with HCB having a polarizability volume of $\approx 6 \times 10^{-24} \text{ cm}^3$, which is 5–6 times lower than commonly detected dyes, such as R6G and MB ($\approx 30\text{--}40 \times 10^{-24} \text{ cm}^3$).

Surface-curvature effect

First, we investigated the SERS detection of HCB (10^{-6} M) on non-porous and curvature-modulated amorphous a-Rh–Se MNs. The tested

substrates included three curvatures: high (a-Rh–Se-S, 0.063 nm^{-2}), medium (a-Rh–Se-M, 0.010 nm^{-2}), and low (a-Rh–Se-L, 0.0059 nm^{-2}) degrees. SERS spectra of HCB show peaks at 220, 376, 1231 and 1523 cm^{-1} similar to Raman spectra (Supplementary Fig. 26) and a few new peaks at 247, 320, 620, 945, and 990 cm^{-1} potentially assigned to semiconductor–analyte complex (Fig. 4a). The increase in pore size and decrease in curvature degree led to a 20.7-fold increase in adsorption capacity of HCB measured in aqueous solution after overnight premixing (Fig. 4b). Typically, an increase of surface area and adsorption capacity lead to the increase of SERS intensity because more molecules of analyte are in proximity to active spots for molecule–substrate interactions⁴⁰. For example, Zhang and colleagues reported ZnO coating by a higher surface area layer for enrichment of non-absorbing molecules by ZIF-8 shells, where the SERS performance is achieved by adsorption control³². However, in our case, a-Rh–Se-L with the lowest surface area provided the highest EF of $>4 \times 10^3$ compared to a-Rh–Se-M and a-Rh–Se-S. We measured HCB concentrations in the range of $10^{-9}\text{--}10^{-4} \text{ M}$ on a-Rh–Se-S, -M, and -L substrates to directly compare substrate-dependent sensing performance. For each variant, in addition to EF, we evaluated standard deviation (SD), and signal-to-noise ratio (SNR) to assess not only amplification strength but also signal reproducibility and analytical reliability (Supplementary Fig. 27 and Supplementary Table 3). Signal variability remains moderate across the series (SD = 8.8–11.8%), while SNR ranges between 8.47 and 11.44. This indicates that key parameters for efficient photo-induced charge transfer (PICT) within CEM for a-Rh–Se are not just limited to surface area.

Therefore, we investigated the relationship between the electronic structure of curvature a-Rh–Se and its EF HCB performance. Specifically, the work function (Φ), measured by Kelvin probe force microscopy (KPFM; Supplementary Fig. 22) and the *d*-band center (ϵ_d), derived from XPS (Supplementary Fig. 20), are correlated with EF HCB (Fig. 4c and Supplementary Fig. 28). Previously, CEM performance was

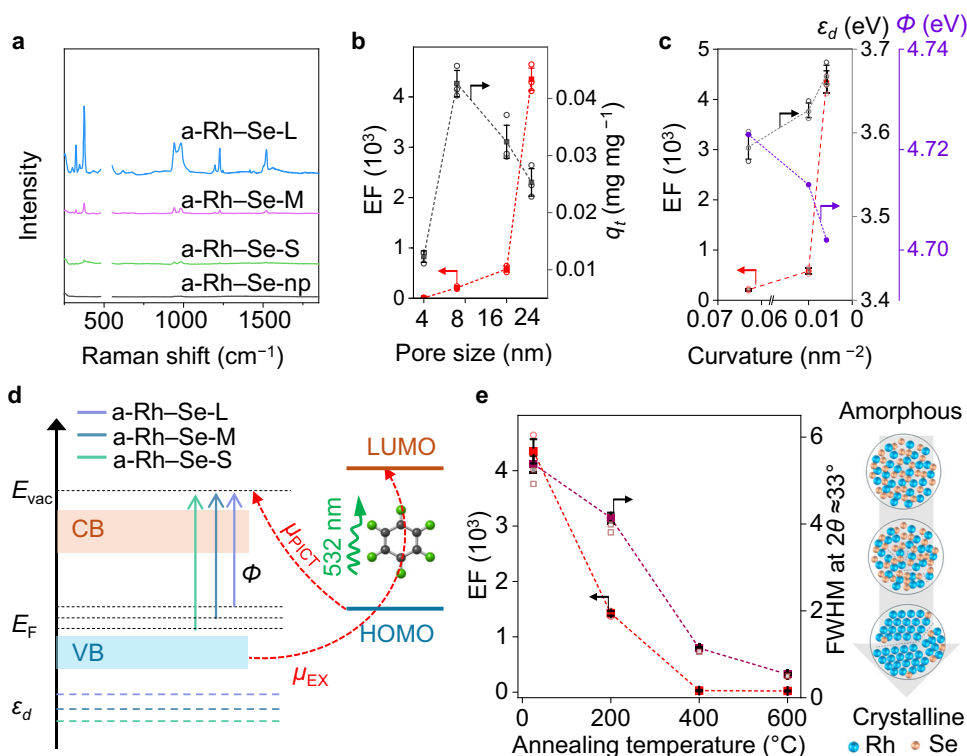


Fig. 4 | Probing SERS sensing of HCB on a-Rh-Se-S/M/L with different curvature degrees. **a** Raman spectra of hexachlorobenzene (HCB) adsorbed on a-Rh-Se-S, a-Rh-Se-M, a-Rh-Se-L, and a-Rh-Se-np. **b** Correlation between pore size, HCB enhancement factor (EF) and HCB adsorption capacity (q_t). **c** Correlation between curvature, HCB EF and d -band center (ϵ_d) and work function (Φ). **d** Schematic illustration of the HCB CEM on a-Rh-Se, highlighting the role of electronic structure

descriptors. a-Rh-Se-S/M/L exhibit varying valence band (VB), CB, E_F , Φ , and ϵ_d (PICT: photo-induced charge transfer; EX: electronic excitation; E_{vac} : energy of the vacuum level). **e** Evolution of HCB SERS EF with variation of annealing temperature/crystallinity of a-Rh-Se (XRD patterns and schematic local structures). Data in (**b**, **c**, **e**) are presented as both individual data points and mean $\pm$ standard deviation (SD) ($n=3$ independent measurements). Source data are provided as a [Source data](#) file.

correlated with electronic structure in the context of aligning the substrate's Fermi level (E_F) (conduction band (CB) and valence band (VB) positions) with the analyte's HOMO or LUMO (highest occupied/lowest unoccupied molecular orbital). However, ϵ_d and Φ are overlooked, which are critical for understanding charge transfer and orbital hybridization. As shown in Supplementary Fig. 20, ϵ_d shifts far away from 3.588 eV (relative to E_F) in the a-Rh-Se-S to 3.670 eV in the a-Rh-Se-L. The trend for Φ is opposite, a-Rh-Se-L with a lower Φ of 4.702 eV, resulting in the highest EF HCB. This trend can be explained by the d -band theory for catalysis developed by Nørskov⁴², which states that transition metals' partially filled d orbitals govern adsorption strength and catalytic activity by tuning d -band position and width. Similarly, ϵ_d position shift in a-Rh-Se-L optimizes the alignment of Rh d -electron states available for excitation by Raman laser (Fig. 4d). This enhances the probability of forming hybridized electronic states between a-Rh-Se-L and HOMO/LUMO of HCB. This orbital overlap facilitates resonant charge transfer and strengthens the Raman polarizability of HCB, thus amplifying its Raman signal.

Previously, Lin et al. showed that the lower Φ enabled more efficient interfacial charge transfer between semiconducting Cu₂O and analytes⁴³. We confirmed this trend on a-Rh-Se-L, where large pores have lower Φ and upward-shifted E_F relative to the vacuum level, reducing the energy barrier for carrier injection into the LUMO of HCB. This improved energy alignment makes carrier transfer to HCB energetically favorable under 532 nm excitation, further reinforcing the CEM (Fig. 4d).

Therefore, we demonstrate that electronic interactions dominate surface area effects in semiconducting a-Rh-Se. Despite reduced surface area at larger pore sizes, the increased density of low-curvature defects and low-coordinated Rh-Se sites leads to a lower Φ and a downshifted ϵ_d relative to E_F . These interface transformations elevate

the E_F , synergistically optimizing the energy alignment between the electronic structure of a-Rh-Se-L and the frontier orbitals of HCB, enabling more efficient PICT under illumination.

Crystallinity modulation

The crystallinity of a-Rh-Se-L was varied via post-annealing temperature (25–600 °C) as confirmed by XRD (Supplementary Fig. 23), TEM and SAED patterns (Fig. 3b–d). As a descriptor of crystallinity, the full width at half maximum (FWHM) of the XRD signal at $2\theta = 33.0^\circ$, 33.0° , 33.4° , and 32.9° for a-Rh-Se-L, Rh-Se-200, Rh-Se-400, and Rh-Se-600 was chosen, respectively (Supplementary Table 2 and Fig. 4e). Smaller FWHM indicates more crystalline material commonly obtained at higher temperature, while larger FWHM indicates the amorphous states of material. It has been recently reported that the amorphous engineering of semiconductors has a significant effect on enhancing SERS activity, which provides opportunities to bypass the bottleneck of the low SERS activity of crystalline semiconductors⁴⁰. However, the effect of this amorphousness remains poorly understood, representing a gap in current knowledge regarding the SERS performance of semiconductors.

We found that increasing the annealing temperature of a-Rh-Se-L and higher crystallinity decreased the HCB EF with negligible Raman activity of the crystalline sample (Fig. 4e). This confirms that amorphous, defect-rich a-Rh-Se is crucial for enabling efficient charge transfer to HCB, likely due to the presence of disorder-induced binding sites and electronic states that facilitate easier carrier excitation. Importantly, this contrasts with noble metal SERS, where crystallinity is often favored because of spectrally sharper plasmon resonances and stronger field localization on crystalline material⁴⁴.

To rationalize observed effects of amorphousness on SERS performance, Rh₂₀Se₈₀ structures with different degrees of

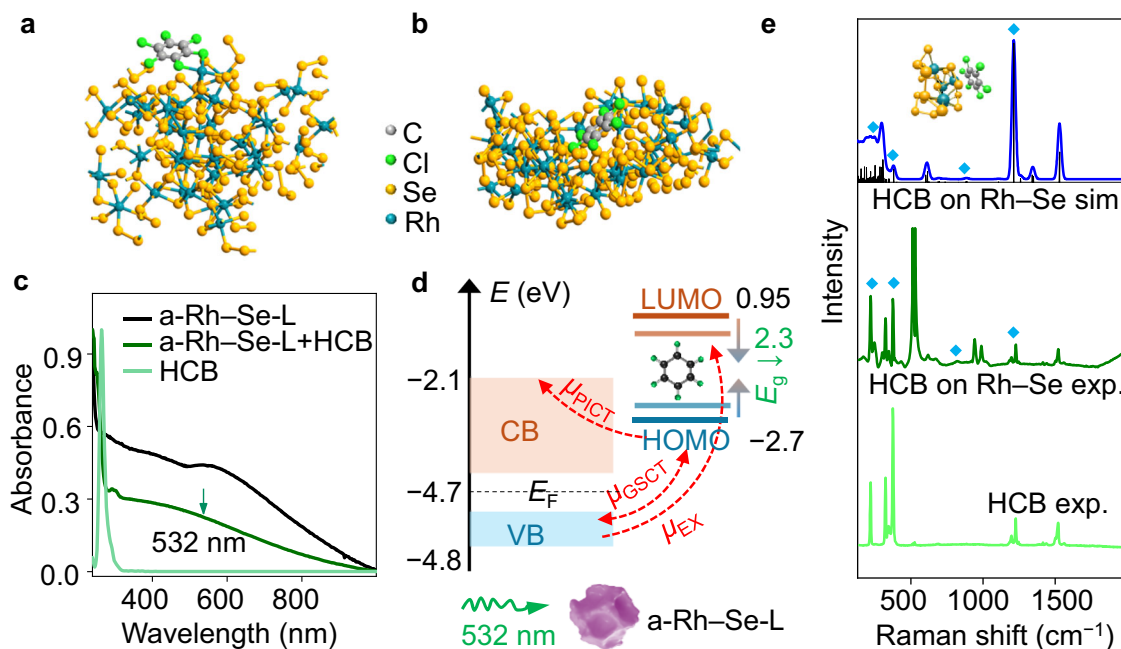


Fig. 5 | DFT adsorption models of HCB at a-Rh-Se. **a** Rh–Se coordinated (low amorph), **b** Rh–Se (highly amorph), **c** UV–vis spectra of a-Rh–Se–L, HCB and mixture a-Rh–Se–L+HCB in methanol and **d** tentative mechanism of the SERS enhancement of HCB on a-Rh–Se substrates via multiple charge transfer pathways that collectively contribute to the CEM. **e** Comparison of experimental (exp.)

Raman spectrum of bulk HCB and SERS spectrum of HCB adsorbed on RhSe, together with corresponding DFT simulation (sim.) spectra of free HCB and HCB@RhSe (insert: optimized DFT cluster models of HCB adsorbed on RhSe, illustrating interfacial binding geometry used for vibrational analysis). Source data are provided as a [Source data](#) file.

amorphousness were modelled using classical molecular dynamics (MD) simulations. The bulk periodic structures were generated using a 200-atom $\text{Rh}_{20}\text{Se}_{80}$ model with randomized atomic positions, and annealed at various temperatures via MD, using the universal CHGNet⁴⁵ force field to obtain two structures with different crystallinity (Supplementary Fig. 29). It is worth noting that the selection of annealing temperatures is not aimed at simulating specific experimental protocols, but rather at generating a series of structural models exhibiting systematically varied degrees of amorphousness. These disordered models reflect the experimentally generated amorphous structures of porous $\text{Rh}_{20}\text{Se}_{80}$.

The average radial distribution functions (RDFs) for Rh–Rh, Se–Se, and Se–Rh pairs reveal clear structural evolution of Rh and Se species with increasing simulated annealing temperature (Supplementary Fig. 30). At lower temperatures (thicker lines), sharp and well-defined peaks indicate strong short-range order, characteristic of amorphous materials with local coordination. As the temperature increases (thinner lines), the RDF peaks broaden and weaken, reflecting enhanced atomic mobility, partial bond disruption, and loss of coordination order. This trend signifies a transition toward a more disordered system with decreased crystallinity. The first Se–Rh peak (≈ 2.4 Å) remains dominant, whereas the Rh–Rh peak is less prominent, highlighting the persistence of local chemical bonding despite the growing disorder at longer distances. The presence of distinct secondary peaks is only observed in the low-temperature model. We chose two model surfaces with different degrees of amorphousness and further named them as a-Rh–Se (low amorph) and a-Rh–Se (high amorph). The adsorption energies are strongly favorable and spontaneous in all cases examined. The most stable adsorption for HCB occurs inside a surface binding pocket of a-Rh–Se (low amorph), exhibiting a very strong interaction of -8.7 eV (Fig. 5a). For adsorption at high amorph, the binding energy is -3.3 eV (Fig. 5b). It should be noted that while the low-amorphous model exhibits a higher absolute binding energy, this likely corresponds to a specific, high-coordination binding pocket identified during the site-selection process. This

localized energy minimum is attributed to the more compact nature of the low-amorphous surface, which allows for increased atomic coordination around the analyte. However, we should note that adsorption is favorable and spontaneous in both models. Thus, the experimental observation that the highly amorphous sample delivers superior SERS enhancement suggests that Raman activity is not solely governed by the thermodynamic stability of a single binding site, but rather by the collective electronic environment of the disordered surface, including its lower work function and optimized *d*-band alignment, which facilitate broader charge-transfer efficiency across the substrate. In addition, to probe different types of resistant analytes, additional molecules were also modelled in the expected most favourable configuration to determine if the strong binding trends remained consistent across different aromatic adsorbates (Supplementary Fig. 31). In fact, comparison of our models with anthracene shows a very similar adsorption behaviour, which is also strong and spontaneous with adsorption energies of -9.1 eV for low amorph and -2.6 eV for high amorph models. The adsorption behaviour of highly symmetric aromatic adsorbates, such as HCB and anthracene, has also been compared with MB (Supplementary Fig. 32), a molecule that has been broadly studied and is well known to be easily adsorbed^{28,46}. In this case, the adsorption is also found to be very strong across all models (-12.1 eV in low and -4.8 eV in highly amorphous), which is in line with the values found for the other compounds.

This confirms that local disorder enhances HCB–substrate interactions, in agreement with experimental trends: a stronger SERS signal correlates with lower work function and a highly amorphous surface. The relatively low polarizability of HCB (6×10^{-24} cm³) indicates that efficient charge transfer is essential for inducing chemical enhancement. Among the configurations, the strongest adsorption on the amorphous surface likely represents the most favorable geometries for PICT and thus the highest SERS activity. To further quantify the interfacial interaction and electron transfer upon HCB adsorption, Mulliken population analysis⁴⁷, which estimates electron density distribution among atoms, was performed (Supplementary Table 4). In

the isolated state, HCB exhibits a neutral-like distribution with Cl atoms at +0.07 e. Upon adsorption, a significant shift in charge is observed across both models, confirming substantial electron donation from the a-Rh–Se surface to the analyte's C–Cl bonds. Specifically, the average charge of Cl atoms increases to +0.18 e and +0.12 e for the low- and high-amorphous models, respectively. This substantial charge redistribution confirms the formation of a strong semiconductor–analyte complex, providing the necessary ground-state coupling for the CEM.

Tentative mechanism

The absorbance suppression and the appearance of a new peak at 290–300 nm observed in ultraviolet–visible spectroscopy (UV–vis) spectra after mixing HCB and a-Rh–Se suggests a change in electronic structure (Fig. 5c). This spectral evolution indicates the formation of molecule–substrate interfacial states resulting from adsorption-induced electronic coupling. Upon adsorption of HCB onto the a-Rh–Se–L surface, interfacial interactions lead to an energetic alignment of the HCB HOMO (−2.7 eV relative to E_F) and LUMO (0.95 eV relative to E_F) with the substrate, resulting in a reduced energy bandgap (E_g) from 3.6 to 2.3 eV (Supplementary Table 5). This alignment enables PICT, whereby the HCB molecular orbitals accept electrons from the photoexcited Rh–Se CB or valence d-states. This leads to a depletion of available photoactive states in Rh–Se, causing an overall reduction in absorbance at the visible range. The experimental E_g of a-Rh–Se was determined to be 2.67 eV from Tauc plot analysis. The E_F location was determined at $\Phi = 4.702$ eV (Supplementary Fig. 22), and the VB onset was measured by XPS to be 0.1 eV below E_F . This places the VB maximum at −4.81 eV and the CB minimum at −2.14 eV with respect to the vacuum level. The density functional theory (DFT) LUMO level of HCB after adsorption is ≈ -1.5 eV, placing it energetically accessible for electron population from substrate states under 2.33 eV excitation and enabling efficient electron transfer from the substrate to the molecule under 2.33 eV laser excitation (Supplementary Table 5).

To further clarify the role of excitation wavelength, Raman spectra obtained under 473, 532, and 633 nm excitation show unchanged Raman band positions but strongly wavelength-dependent signal intensities and relative mode ratios (Supplementary Fig. 33 and Supplementary Table 6). For example, the normalized intensity ratio I_{1228}/I_{376} changes from 0.995 at 473 nm to 0.731 at 532 nm and further to 0.669 at 633 nm excitation, where such wavelength-dependent variations in relative band intensities indicate excitation-dependent modification of vibrational polarizability via charge-transfer transitions rather than uniform electromagnetic amplification. The strongest enhancement and highest signal-to-noise ratio are obtained under 532 nm excitation, while signals decrease significantly at 633 nm, and spectra measured at 473 nm resemble the bulk Raman response without pronounced mode selectivity. Such excitation-dependent enhancement indicates that Raman amplification efficiency is governed by photon-energy matching with interfacial electronic transitions rather than purely electromagnetic field enhancement. Consequently, selective enhancement of specific vibrational modes arise from excitation-dependent modulation of molecular polarizability via charge-transfer transitions.

The observed SERS enhancement of HCB on a-Rh–Se–L substrates can be attributed to multiple charge transfer (CT) pathways that collectively contribute to the CEM (Fig. 5d). First, interfacial ground-state charge transfer ($\mu_{\text{GSC T}}$) occurs via static orbital hybridization between the HCB HOMO and low-lying unoccupied states of Rh–Se. Mulliken population analysis confirms this interaction, with Cl atoms showing a charge increase upon adsorption, indicating electron donation from the substrate. Second, interfacial photo-induced charge transfer ($\mu_{\text{P I C T}}$) is enabled by the energetic alignment between the CB of Rh–Se and the HOMO of HCB (−0.8 eV, DFT data), allowing excited electrons to transiently populate the analyte's antibonding orbitals under 2.33 eV

laser excitation. This process is facilitated by the elevated ϵ_d and lower Φ of the more disordered, porous Rh–Se surfaces. Lastly, intramolecular electronic excitation ($\mu_{\text{E X}}$) within HCB itself may also contribute, as its HOMO–LUMO gap closely matches the laser energy, further enhancing the polarizability via resonance. These synergistic CT interactions, both static and dynamic, explain the pronounced SERS signal amplification observed on highly amorphous Rh–Se substrates.

To elucidate the origin of chemical enhancement, we compared HCB-derived signals on Raman spectra, SERS on a-Rh–Se and simulated using hybrid-DFT calculations (Fig. 5e and Supplementary Fig. 34). DFT vibrational spectra were computed using both the isolated molecule and adsorption models on non-periodic cluster structures. The comparison between experiment and simulation reveals adsorption-induced vibrational modifications consistent with interfacial electronic coupling. The C–Cl shear mode appears additionally at 247 cm^{-1} upon adsorption (in addition to 220 cm^{-1} assigned to bulk HCB), indicating vibrational constraint. The 376 cm^{-1} band shows no measurable frequency shift between bulk Raman and SERS, yet its relative intensity decreases in SERS. The aromatic ring-breathing mode shifts from 1229 to 1216 cm^{-1} , reflecting perturbation of the π -electron system. Importantly, a new band near 880 cm^{-1} appears exclusively for adsorbed HCB. The adsorption-specific mode is attributed to symmetry breaking at the Rh–Se interface. Free HCB possesses inversion symmetry, but adsorption introduces an asymmetric surface–vacuum environment, relaxing Raman selection rules and enabling previously forbidden or weak modes to gain intensity. Simultaneously, interfacial charge-transfer coupling modifies the molecular polarizability tensor, selectively amplifying vibrational modes under excitation energies resonant with interfacial electronic transitions. The strong agreement between experimental and simulated spectral evolution therefore provides direct spectroscopic evidence that SERS enhancement in a-Rh–Se originates from charge-transfer-driven chemical enhancement rather than purely electromagnetic amplification. Such enhancement is consistent with the charge-transfer mechanism observed in previous semiconductor-based SERS studies^{48,49}.

To understand how the electronic landscape supports this mechanism, we examined the projected density of states (PDOS). PDOS analysis reveals that the Rh 4d-band, centered ≈ -1 to -3 eV, shows only minor depletion with increasing amorphousness (Supplementary Fig. 35), suggesting that bulk electronic structure is largely preserved. Upon HCB adsorption, Cl 3p and C 2p states broaden and hybridize with Rh–Se orbitals, producing interfacial states close to E_F that could facilitate excitation-dependent electron transfer pathways. We should note that while for Rh–Se our DFT calculations show metallic behavior for all atoms, with a local minimum located at E_F , the experimental outcomes suggest a semiconducting behavior arising probably from dynamic effects. This might be due to charge localization via polaron formation, where electron-phonon coupling in the disordered network could open an optical gap despite the metallic band structure. Despite this discrepancy, the atomic-level geometries and adsorption models remain representative of the short-range order within the material. Upon HCB adsorption, distinct Cl 3p and C 2p states hybridize with RhSe orbitals, especially on a-Rh–Se (high amorph). This hybridization, accompanied by a pronounced reduction of the molecular HOMO–LUMO gap (from 3.63 to 2.31 eV), supports a CEM via PICT. Unlike conventional d-band theory systems (e.g., Pt, Pd), where ϵ_d governs reactivity, here the disorder-induced local states at the interface appear more relevant to SERS activity.

Quantitative detection for HCB

The quantitative SERS performance was evaluated over an HCB concentration range of 10^{-4} – 10^{-10} M⁵⁰. The band at 375 cm^{-1} (C–Cl) was used as the analytical marker to construct a calibration curve (Fig. 6a, b), which exhibited a linear response over four orders of magnitude. The LOD, calculated based on calibration curve (using

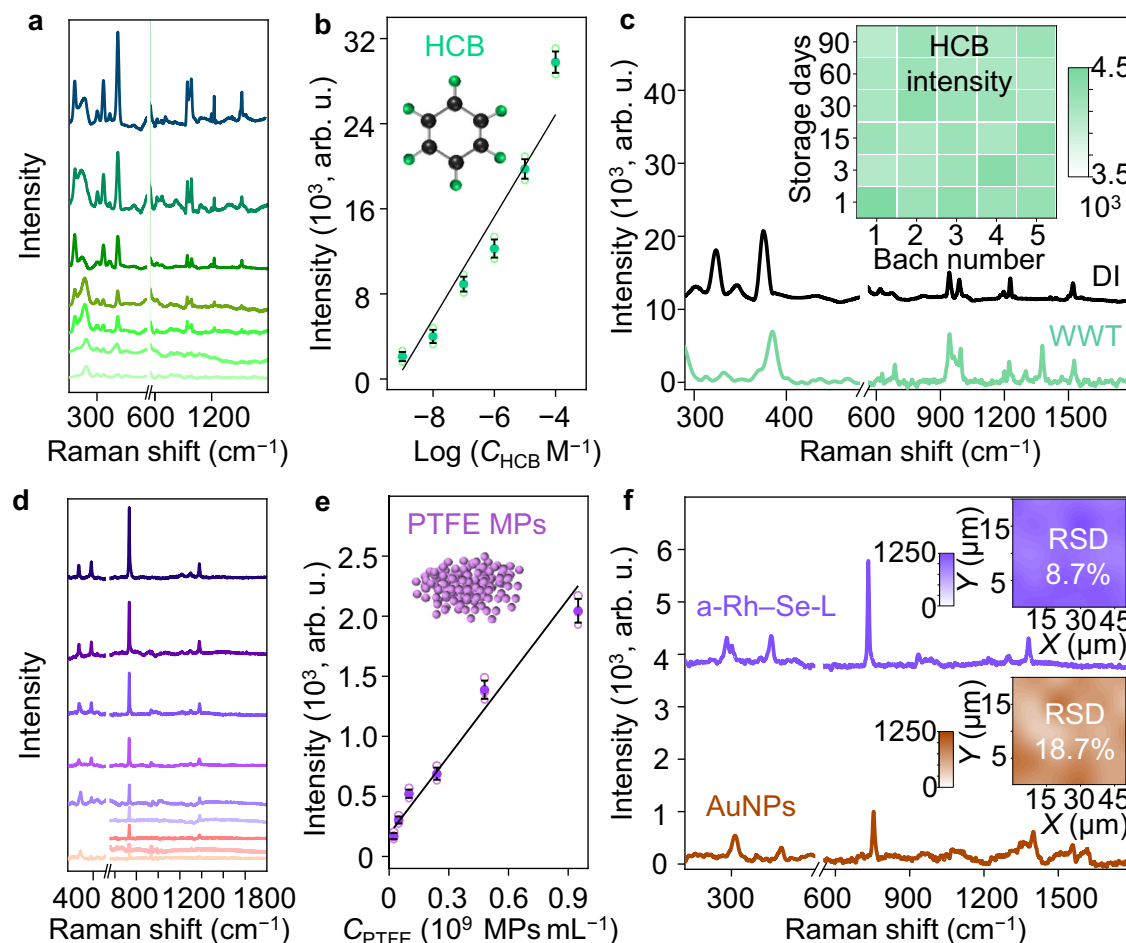


Fig. 6 | SERS performance of a-Rh-Se-L substrates for HCB and PTFE microplastics (MPs) detection in a real wastewater (WWT) sample. **a** Quantitative SERS sensing of HCB using concentrations 10^{-4} to 10^{-10} M. **b** The corresponding characteristic HCB peak intensities at 375 cm^{-1} as a function of the concentration (C_{HCB} : the concentration of HCB). **c** SERS spectra of HCB (10^{-6} M) detected in deionized (DI) water and WWT matrix; inset shows long-term storage stability (90 days, 5 batches), confirming reproducibility (RSD = 2.55%). **d** Quantitative SERS sensing of PTFE MPs using concentrations 0.01 to 10^9 particles mL^{-1} . **e** The

corresponding characteristic PTFE MPs peak intensities at 734 cm^{-1} as a function of the concentration. **f** SERS spectra of PTFE MPs (0.5×10^9 particles mL^{-1} in WWT) on a-Rh-Se-L versus AuNPs substrates. Insets show SERS maps of intensity at 734 cm^{-1} across a $20 \times 50\text{ }\mu\text{m}^2$ area, with calculated relative standard deviation (RSD) values of 8.7% (a-Rh-Se-L) and 18.7% (AuNPs), indicating higher signal reproducibility on a-Rh-Se-L. Data in (b, e) are presented as both individual data points and mean $\pm$ SD ($n = 3$ independent measurements). Source data are provided as a [Source data](#) file.

residual standard deviation of a regression line⁵¹, was determined to be 6.2×10^{-9} M, confirming the high sensitivity of the a-Rh-Se-L towards non-resonant, low-polarizability analyte in trace-level concentrations. To assess real-world applicability, HCB was detected in a wastewater treatment (WWT) sample collected from the TATRA Kopřivnice wastewater treatment facility, Czechia (Supplementary Table 7). This WWT sample was characterized by a chemical oxygen demand (COD) of 153 mg L^{-1} and a biological oxygen demand (BOD_5) of 44.8 mg L^{-1} . The relative high COD/ BOD_5 ratio (≈ 3.4) indicates a substantial fraction of poorly biodegradable matter⁵² (Supplementary Table 7). This makes the sample highly relevant for detecting persistent organic pollutants, such as HCB. Despite matrix complexity, the SERS signal of HCB remained clearly detectable.

To assess long-term sensing stability and reproducibility, we evaluated the SERS response of a-Rh-Se-L substrates for HCB detection in WWT across five independently prepared batches over a period of 90 days (Fig. 6c). The SERS intensity remained highly stable, with a relative standard deviation (RSD) of 2.55%, confirming both temporal and inter-batch reproducibility. Such matrices present a challenging analytical environment because of (i) background of organic matter competing with HCB for adsorption, (ii) potential fluorescence or Raman signal suppression from humic-like substances in WWT

matrix^{53,54}. Unlike noble metal SERS substrates, which often suffer from signal degradation due to surface oxidation/contamination and nanoparticle aggregation^{55,56}, a-Rh-Se-L maintained stable performance for long-term monitoring of trace-level pollutants in complex environmental matrices.

To properly compare the performance of a-Rh-Se and AuNPs (Supplementary Fig. 36), we also performed HCB sensing on AuNPs (Supplementary Fig. 37). The resulting EF of 34,702 was much higher than for a-Rh-Se (up to $>4 \times 10^3$). However, a-Rh-Se samples possess lower signal variability and higher SNR compared to AuNPs (Supplementary Table 3). Thus, while AuNPs provide stronger absolute EM amplification for small molecules, such as HCB, the a-Rh-Se substrates deliver more uniform enhancement and superior analytical stability. This result demonstrates that SERS performance in this system is governed primarily by substrate electronic structure and charge-transfer efficiency rather than pore inclusion effects or purely hotspot-driven EM mechanisms.

Anthracene sensing in industrial wastewater

To further demonstrate applicability beyond chlorinated aromatics, sensing experiments were extended to polycyclic aromatic hydrocarbons (PAHs), using anthracene as a representative pollutant with polarizability volume of $2.67 \times 10^{-23}\text{ cm}^3$. PAHs can occur in industrial

wastewater as a consequence of combustion-related and other industrial activities^{57,58}. As persistent hydrophobic pollutants with limited surface affinity, PAHs, such as anthracene, are typically difficult to detect using conventional semiconductor SERS substrates^{59,60}.

SERS spectra of a-Rh–Se substrates show characteristic anthracene bands at 395 and 1402 cm^{-1} (Supplementary Fig. 38), enabling quantitative detection across concentrations from 10^{-9} to 10^{-4} M. Measurements performed in industrial wastewater obtained from a specialty glass manufacturing facility (Supplementary Table 8) show that anthracene signals remain clearly detectable despite matrix background contributions. Additional Raman bands observed in the wastewater matrix appear at 600–620, 780–820, and 1000–1100 cm^{-1} , associated with silicate network vibrations from glass components, as well as at 1060, 1130, 1295–1305, 1375, and 1440–1450 cm^{-1} originating from hydrocarbon residues of oils and lubricants, while bands near 1600 cm^{-1} arise from aromatic residues and 1640 cm^{-1} correspond to water bending modes (Supplementary Table 9). These background features do not obscure anthracene marker peaks. These results confirm that the a-Rh–Se platform enables the detection of chemically resistant pollutants in realistic industrial water matrices.

Persistent microplastic PTFE sensing

Building on the CEM-driven detection of HCB, we extended the $\text{Rh}_{20}\text{Se}_{80}$ SERS platform to non-adsorbing PTFE MPs with a diameter ≈ 250 nm. SEM imaging combined with EDS elemental mapping (Supplementary Fig. 39) confirms that PTFE particles are deposited on the external mesostructured a-Rh–Se-L surface, with homogeneous fluorine distribution co-localized with the selenium framework. PTFE MPs are a growing concern due to their environmental persistence and potential release from consumer and industrial materials^{61–63}. PTFE presents a challenging target due to its low Raman cross-section and low polarizability volume of $\approx 5 \times 10^{-24} \text{ cm}^3$, even lower than that of HCB. Conventional EM-driven and semiconducting substrates often fail to detect PTFE because (i) minimal affinity to noble metal surfaces, and (ii) there is a general mismatch between the large (hundreds of nm to μm) size of MPs and plasmonic hot spots. We recently reported that such a mismatch limits effective EM field confinement and signal enhancement, necessitating alternative strategies that enable analyte capture and SERS activation⁶³.

The quantitative SERS detection of PTFE MPs consistently showed the characteristic vibrational bands of PTFE at 734 and 1382 cm^{-1} (Supplementary Fig. 40) across a wide concentration range ($0.24\text{--}5 \times 10^9$ particles mL^{-1}) (Fig. 6d, e)⁶⁴. The tested concentration range was selected to evaluate the analytical performance toward submicrometric PTFE particles^{65,66}. The saturation trend was observed at concentrations above 1×10^9 particles mL^{-1} because of surface coverage limitations. At high PTFE loading, the substrate becomes saturated with PTFE particles, leading to crowding, partial signal quenching, and reduced access to enhancement sites. This saturation behaviour likely arises from surface coverage limitations: the a-Rh–Se-L becomes saturated with PTFE, leading to crowding, partial signal quenching, and reduced access to enhancement sites. However, such concentrated MP suspensions could be easily detected by analytical microscopy tools⁶⁷. The calibration curve obtained from sensing in an environmentally relevant concentration range is $0.24\text{--}1 \times 10^9$ particles mL^{-1} , showing a strong linear relationship ($R^2 = 0.996$), indicating reliable quantification capability.

Finally, the SERS performance of a-Rh–Se-L and common 13 nm AuNPs (Supplementary Fig. 36) was compared using 0.5×10^9 particles mL^{-1} PTFE MPs suspension in WWT (Fig. 6f). Each spectrum represents the average acquired across a $20 \times 50 \mu\text{m}^2$ area using intensity at 734 cm^{-1} . The PTFE vibrational mode observed at 756 cm^{-1} on AuNPs appears at 734 cm^{-1} on a-Rh–Se-L, corresponding to a 22 cm^{-1} red shift. On AuNPs in the area of 300–400 cm^{-1} , PTFE modes appear as single, symmetric features consistent with EM-dominated

enhancement. In contrast, a-Rh–Se-L exhibits peak broadening and mode splitting, particularly near 300 cm^{-1} , along with a 5–7 cm^{-1} red shift of the 400 cm^{-1} mode. Variations in vibrational features are attributed to interfacial electronic coupling, supporting a significant CEM contribution on a-Rh–Se-L. CEM can selectively amplify modes coupled to interfacial charge-transfer transitions and may induce small frequency shifts due to surface electronic coupling. The average intensity of PTFE is $\times 1.5$ higher for a-Rh–Se-L than for AuNPs, despite the EM field mechanism of SERS enhancement for noble metals commonly providing higher Raman signal enhancement than CEM.

Within the SERS map, up to $\approx 20,000$ PTFE particles (250 nm) could theoretically fit under dense monolayer conditions. However, at 0.5×10^9 particles mL^{-1} , the estimated number of particles is negligible, indicating that SERS signals depend primarily on particle adsorption onto the substrate rather than on random diffusion through the probing region. Comparative measurements revealed that $\text{Rh}_{20}\text{Se}_{80}$ exhibited higher and more uniform SERS signals, with a RSD of 8.7%, compared to 18.7% for AuNPs (Fig. 6f). This improved reproducibility may reflect a higher surface affinity of PTFE for a-Rh–Se-L, likely due to higher adsorption energy or stronger hydrophobic interactions. In contrast, the hydrophilic and negatively charged AuNPs may repel the PTFE particles, leading to lower adsorption density and greater signal variability.

Overall, amorphous metal–selenide semiconductors, such as a-Rh–Se-L, offer a complementary materials route for SERS sensing of chemically resistant pollutants by emphasizing substrate–molecule electronic coupling rather than hotspot-dominated electromagnetic amplification. Prior studies have demonstrated that microplastics⁶⁸ and other weakly interacting pollutants^{69,70} can be detected using plasmonic SERS platforms, including macroporous Ag foams combined with machine-learning spectral analysis for complex plastic mixtures⁶³ and anisotropic Au nanostar substrates enabling detection of submicron and nanoplastic particles at low mass concentrations⁷¹. However, detection of hydrophobic and resistant contaminants on plasmonic SERS substrates often requires additional interfacial engineering, such as linker-induced nanoparticle junction formation to create adsorption-active hot spots⁶⁹ or in situ extraction and self-assembly strategies using ligand-modified Au nanoparticles to overcome weak molecular affinity and matrix complexity⁷⁰. In this context, amorphous metal selenides provide several general advantages for SERS beyond specific noble-metal systems: (i) improved long-term stability (resistance to oxidation and aggregation), (ii) uniform, substrate-wide enhancement via CEM, driven by high density of accessible low-curvature sites and dangling bonds, (iii) efficient detection of low-polarizability molecules via orbital alignment and PICT, (iv) higher reproducibility and signal consistency in complex matrices like wastewater, (v) stronger particle–substrate affinity, further enhanced by geometric binding pockets that stabilize analyte–substrate interactions, enabling consistent detection of large-size pollutants like microplastics.

Discussion

In this work, we developed a-Rh–Se MNs using a chemical reduction method. The SERS performance of these MNs is significantly influenced by both their surface curvature and crystallinity. Our results show that a-Rh–Se-L with low curvature reduces the energy barrier for charge transfer, promoting efficient energy alignment and carrier injection. This effect is coupled to the material's amorphous character, which introduces disorder-induced electronic states that enhance carrier excitation. Together, reduced surface curvature and amorphization reshape the electronic structure, the *d*-band center and the work function, to promote resonant charge transfer. Consequently, this strategy enables semiconductor-based SERS to detect chemically challenging analytes, including HCB, anthracene and

PTFE MPs, extending SERS capabilities beyond conventional dyes and thiolated probes. Our findings indicate that the surface curvature, together with amorphization, plays a critical role in governing the SERS activity, overturning the traditional SERS assumption that favors high-surface-area substrates. This work deepens our understanding of how a semiconductor's structural parameters govern its SERS activity.

Methods

Materials

All reagents were used as purchased without further purification. Sodium hexachlororhodate (III) (Na_3RhCl_6), selenous acid (H_2SeO_3 , 98%), gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$ trace metals basis), sodium citrate tribasic dihydrate (Na_3CA , $\geq 99.0\%$) and formic acid (HCOOH , $\geq 96\%$) were purchased from Sigma Aldrich. PEO-*b*-PMMA with different molecular weights of PMMA blocks, including PEO₃₅₀₀-*b*-PMMA₁₇₀₀, PEO₁₀₀₀₀-*b*-PMMA₅₅₀₀, and PEO₁₀₅₀₀-*b*-PMMA₁₈₀₀₀ (the subscript numbers indicate the average molecular weight (g mol^{-1}) of the corresponding blocks), were obtained from Polymer Source. THF (99.5%), ethanol (99.5%), methanol (99.5 %), and acetone ($\geq 99.0\%$) were purchased from FUJIFILM Wako Pure Chemical Corporation.

Synthesis of a-Rh-Se-L MNs

The a-Rh-Se-L MNs were synthesized via a wet-chemical reduction approach combined with diblock copolymer micelle assembly. In a typical procedure, 4 mg of PEO₁₀₅₀₀-*b*-PMMA₁₈₀₀₀ was first dissolved completely in 0.4 mL of THF at 70 °C in a vial, followed by cooling to ambient temperature ($\approx 22^\circ\text{C}$). Subsequently, 1.6 mL of deionized water, 4 mL of an aqueous solution containing Na_3RhCl_6 (40 mM) and H_2SeO_3 (40 mM) at predetermined ratios (typical feeding volume is $\text{Na}_3\text{RhCl}_6:\text{H}_2\text{SeO}_3 = 1:3$), along with 1 mL of HCOOH , were added dropwise to the THF solution under gentle stirring (200 rpm). After 5 min of mixing, the reaction system was transferred to an oil bath and maintained at 80 °C for 12 h under static conditions. The resulting products were then collected by centrifugation at $18,000 \times g$, thoroughly washed with a 2:1 acetone-water mixture ($6 \times 30\text{ mL}$), and finally vacuum-dried. The nonporous a-Rh-Se reference was prepared similarly to a-Rh-Se-L MNs, except omitting the diblock copolymer.

Synthesis of Rh-Se MNs with different crystallinity

The Rh-Se MN samples with different crystallinities were obtained by annealing the as-synthesized a-Rh-Se-L at different temperatures (200, 400, and 600 °C) under an inert argon atmosphere. The temperature was increased at a rate of 2°C min^{-1} to the target temperature and maintained for 3 h. The resulting products at 200, 400, and 600 °C were designated as Rh-Se-200, Rh-Se-400, and Rh-Se-600, respectively.

Synthesis of a-Rh-Se-M

The synthesis of a-Rh-Se-M was consistent with the process described for sample a-Rh-Se-L MNs above, with the only difference being the replacement of the polymer (PEO₁₀₅₀₀-*b*-PMMA₁₈₀₀₀) with PEO₁₀₀₀₀-*b*-PMMA₅₅₀₀. The feeding amounts of Na_3RhCl_6 and H_2SeO_3 were 1 and 3 mL, respectively.

Synthesis of a-Rh-Se-S

The synthesis of a-Rh-Se-S was consistent with the process described for sample a-Rh-Se-L MNs, with the only difference being the replacement of the polymer (PEO₁₀₅₀₀-*b*-PMMA₁₈₀₀₀) with PEO₃₅₀₀-*b*-PMMA₁₇₀₀ and the volume of deionized water was changed to 3.2 mL. The feeding amounts of Na_3RhCl_6 and H_2SeO_3 were 1 and 3 mL, respectively.

Synthesis of AuNPs

AuNPs were prepared by a modified Turkevich method⁷². In a 250 mL round-bottom flask, 1 mL of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (100 mg in 10 mL) and 2.5 mL of Na_3CA (284.9 mg in 25 mL) were added to 100 mL of boiling water. Heating continued for 10 min during which time the solution became red. After cooling to room temperature, AuNPs were purified from Na_3CA by centrifugation and washing with a 1:3 water-methanol mixture ($7050 \times g$, 30–60 min). After each centrifugation cycle, AuNPs were sonicated for 1–2 min. The resulting precipitate of AuNPs was resuspended in 50 μL of methanol, which was deposited on a silica slide ($0.5 \times 0.5\text{ cm}^2$) by drop-casting for further Raman study.

Characterizations

The elemental composition of a-Rh-Se MNs was analyzed by ICP-OES using an Agilent 5800 spectrometer. Morphological characterization was conducted with a Zeiss Gemini SEM 560 scanning electron microscope operated at 10 kV, equipped with a Bruker 5060F flat quad EDS detector for elemental mapping. Surface potential measurements were performed using KPFM on a Bruker Dimension Icon system. TEM and HAADF-STEM with EDS were performed on a Talos F200X G2 (Thermo Fisher Scientific) operated at 200 kV in nanoprobe mode, with a beam convergence angle of 20 mrad and a HAADF detector collection range of 60–200 mrad, equipped with a Super-X EDS detector. For STEM tomography, tilt series were acquired over a range of -65° to $+65^\circ$ in 2° increments and reconstructed using the simultaneous iterative reconstruction technique (SIRT, 10 iterations) in Tomviz. Segmentation and 3D rendering were performed in 3D Slicer, and the resulting models were processed in Autodesk Fusion 360 for visualization. XPS measurements were conducted on a Thermo Scientific K-Alpha+ system with a monochromatic Al K_α X-ray source (1486.6 eV), and binding energies were calibrated against the C 1s peak at 284.8 eV. All XPS samples underwent identical preparation and measurement protocols. Crystalline structure was examined by XRD on a Rigaku SmartLab diffractometer using $\text{Cu } K_\alpha$ radiation (40 kV, 30 mA), with data collected from 20° to 90° (2θ) at a step size of 0.02° . SAXS measurements (Rigaku NANO-Viewer) were employed to determine the pore-to-pore distance. Additionally, nitrogen adsorption-desorption isotherms were obtained at 77 K using a BELSORP-mini (BEL, Japan), and pore size distributions were derived from the Barrett-Joyner-Halenda model. XAS measurements were conducted in beamline TPS 44A, quick-scanning X-ray absorption spectroscopy, NSRRC, Taiwan. The synchrotron X-ray energy ranges from 4.5 to 34 keV (depending on the target central elements). The focused spot size is $10 \times 10\text{ }\mu\text{m}^2$. All the powder samples were ground into fine powder, concealed with Kapton tape, and fixed on the sample holder.

SERS measurements

Preparation of SERS substrate and analyte deposition. The suspension (2 mg mL^{-1}) of powder of a-Rh-Se was prepared in methanol and deposited onto a silicon wafer ($0.5 \times 0.5\text{ cm}^2$) by drop casting. For analyte deposition to the SERS substrate, a-Rh-Se suspension (0.1 mL) was premixed with HCB solution or a PTFE MP dispersed solution (0.9 mL) in specific concentrations for 1 h and then centrifuged to concentrate it to 0.1 mL of a-Rh-Se. The sample was prepared by drop casting onto a silicon wafer ($0.5 \times 0.5\text{ cm}^2$).

Raman spectroscopy measurements. Raman spectra of the MPs were collected on an inVia™ confocal Raman microscope (Renishaw, United Kingdom) with 532 nm (6 mW, 10 s for each exposure) and a resolution of 2 cm^{-1} (600 grooves mm^{-1} grating) spanning 2000 to 200 cm^{-1} . The spectra were acquired using a $20\times$ objective and a 40 s collection time. In mapping mode, the objective was parked over the substrate and then scanned, with a collection time of 40 s per point.

Additional measurements have been done using LabRAM ARAMIS (Horiba, Japan) with red (633 nm) and blue (473 nm) lasers at a power density of 14 and 20 kW cm⁻², respectively. The spectra were acquired using a 20× objective and a 40 s collection time. For the calculations of EFs, three independent measurements were acquired and intensities were used with SD calculated from N spectra

according to the relation $SD = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N}}$, where x is the intensity of the Raman signal, $\bar{x}$ is the mean of the intensities, and N is the number of spectra used.

EF calculation. Calculation of the SERS EF was performed according to the standard relation: $EF = \frac{I_{SERS}/C_{SERS}}{I_{RS}/C_{RS}}$, where the I_{SERS} and I_{RS} represent the Raman scattering intensities on SERS-active and reference silicon surfaces, and C_{SERS} and C_{RS} are the corresponding concentrations of analyte. For measuring the I_{RS} on silicon, 10⁻¹ M of HCB and PTFE MPs aqueous solution was used. To accurately estimate the number of molecules excited by the confocal microscope, a 20× objective lens with a 1.1 μm beam waist was illuminated through a container with a depth of 3 μm. Assuming the Gaussian beam excites a volume that is roughly the shape of a cylinder, we can estimate the volume excited by the beam using $V = 0.5 \times D \times \pi \times h$, where D is the beam waist, and h is the height of the container. By multiplying the concentration of the solution (in molecules μm⁻²) by the beam volume, we can estimate the number of molecules excited in the Raman reference measurement (C_{RS}).

Calculation of LOD. The calibration curve was plotted using analytical solutions of HCB and PTFE in different concentrations in a 3:1 water-methanol mixture. The spectra were measured with a 40 s accumulation time for each measurement using a 532 nm laser (6 mW). The LOD was calculated using a calibration curve (using residual standard deviation of a regression line). The residual standard deviation of a regression line or the standard deviation of the y-intercepts of regression lines was used as the standard deviation. The RSD of the signal was calculated according to relation RSD calculation $RSD = (\frac{SD}{\bar{x}}) \times 100\%$, from three spectra according to the relation, where $\bar{x}$ is the mean of the intensities of the Raman signal (376 and 736 cm⁻¹ for HCB and PTFE MPs, respectively).

Preparation of PTFE MP solutions in WWT. HCB was dissolved in the WWT matrix, whereas PTFE MPs were dispersed to obtain the specified particle concentration. The water was collected on 20.03.2025, and analyzed by ALS Czech Republic, s.r.o. under order number PR2561392. The matrices were raw water from the TATRA Kopřivnice site. The analysis was conducted in accordance with the internal quality control standards of ALS ČR, following ČSN EN ISO/IEC 17025:2018. The composition of the sample is given in Supplementary Table 7.

Preparation of anthracene solutions in industrial wastewater. Anthracene stock solutions were prepared in ethanol (analytical grade) and subsequently diluted to the desired concentrations (10⁻⁹–10⁻⁴ M) using industrial wastewater. The wastewater sample was collected on 20.03.2025 and analyzed by ALS Czech Republic, s.r.o. under order number PR2561378. The water was collected from SCHOTT AG wastewater treatment facility. The analysis was performed in accordance with internal quality control standards of ALS ČR following ČSN EN ISO/IEC 17025:2018. The compositions of sample were given in Supplementary Table 8.

Storage stability test. The stability of SERS substrates was estimated under the normal storage conditions in air at 23–25 °C. The a-Rh–Se was used for HCB (10⁻⁶ M) detection, and then the sample was stored up to 3 months after preparation and measured by Raman in experimental conditions as described above.

Computational methods. Bulk amorphous RhSe, containing 80 at.% Se and 20 at.% Rh (henceforth a-Rh–Se), was prepared using classical MD simulations. The LAMMPS package was used to run the relaxations⁷³. The atomic interactions were obtained from the universal CHGNET version 0.3 force field⁴⁵, which is trained on data from different RhSe binary polymorphs. The different amorphous structures were produced by annealing a 200-atom (160 Se and 40 Rh) system with randomly distributed in a periodic crystalline cubic box. The Nosé–Hoover thermostat in its isothermal-isobaric form (NPT) was set to a constant pressure of 1 atm, with a time step of 1 fs. To intentionally produce structural models with different degrees of amorphousness, a common initial system was annealed at temperatures of 100 and 2000 K and equilibrated for 50 ps, until reaching structural equilibration of the models at their final stages. This procedure leads to two equilibrated cubic systems, in which the densities and crystallinity are inversely proportional to the annealing temperature. The pair distribution function was obtained from sampling every 10 steps over the final 5000 steps.

The surface models were then cleaved from the bulk at a plane parallel to one of the box sides, where a large vacuum layer is introduced. Whenever possible, and with the objective of creating slabs featuring binding pockets for the molecules, the surfaces were intentionally cleaved at regions next to voids formed in the periodic structures. We expect these adsorption models to be more relevant and comparable with the experimental measurements.

The slabs were relaxed using the SIESTA DFT code (v5.2)^{74,75}. Initial relaxations of the slabs were directly performed via DFT due to the force field's lower reliability in vacuum systems. Hexachlorobenzene and MB were then individually adsorbed onto the RhSe surface, with various orientations and locations explored to find the most energetically favoured conformation for further analysis. Models were initially relaxed using a 500 Ry mesh cutoff and a 0.02 Ry energy shift, while the most stable candidates were refined at 800 and 0.005 Ry, respectively. All calculations employed double-zeta polarised basis sets, the PBEsol exchange-correlation functional⁷⁶, and Pseudodojo pseudopotentials⁷⁷. Long-range interactions were accounted for using Grimme's D3 method⁷⁸. Electronic convergence criteria were set at 10⁻⁶ eV for energy differences and 0.02 eV Å⁻¹ for forces. In-plane lattice parameters were fixed, while the atomic coordinates and the out-of-plane cell dimension were allowed to relax. A 2 × 2 × 1 Monkhorst-Pack k-point mesh was used, with no replication along the vertical axis. Atomic figures and visualizations were generated using the QuantumATK builder package⁷⁹.

To investigate the vibrational properties of the Rh–Se system with high precision, a two-stage modeling approach was employed. Initially, Rh₅Se₂₀ clusters were relaxed within a periodic framework using SIESTA^{74,75} to establish stable local geometries within a bulk/surface context. These pre-relaxed structures were then extracted and treated as isolated clusters for further relaxation and vibrational analysis. This cluster-based transition allows for the deployment of hybrid functionals and triple-zeta basis sets, which provide the necessary accuracy for Raman intensity simulations that are otherwise computationally prohibitive in large systems with periodic boundary conditions.

All non-periodic calculations were performed using the ORCA v6 suite⁸⁰. Geometry optimizations and frequency analyses were conducted using the B3LYP hybrid functional^{81,82}. The electronic environment was described using the def2-TZVP basis set. For rhodium ($Z = 45$), scalar relativistic effects were accounted for via the def2-ECP effective core potential. Se, C, and Cl atoms were treated using an all-electron description. To accurately capture the non-covalent interactions between the HCB and the cluster, Grimme's D3 dispersion correction with Becke–Johnson damping was applied^{78,83}. To ensure high-fidelity Raman spectra, the numerical differentiation increment for the Hessian was tightened to 0.001 Bohr. Molecular geometries and vibrational modes were visualized using the Avogadro2 software

package⁸⁴, applying a broadening to bridge the gap between discrete DFT peaks and experimental observations.

Reporting summary

Further information on research design is available in the Nature Portfolio Reporting Summary linked to this article.

Data availability

The raw data generated from the atomistic simulations in this study are publicly available via NOMAD⁸⁵. Additional data are available from the corresponding authors upon reasonable request. Source data are provided with this paper.

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Author contributions

Y.K. and O.G. co-supervised the project, performed the sample synthesis, structural characterization, SERS measurement, and drafted the paper. Y.T. did part of the SEM and Raman experiments. L.F. and J.Z. carried out the AFM measurements. N.C.-R.C., W.-H.H., M.-H.Y., and K.C.-W.W. performed the XAFS measurements and fitted the data. J.G.M. carried out the atomistic simulations. S.J. performed SERS measurement. J.H. performed the TEM, STEM-EDS, and STEM tomography measurements. Y.G., X.L., and Y.Z. carried out the XPS and BET measurements. Y.A. and M.V. revised the manuscript. Y.Y. conceived the idea, supervised the project, discussed the experimental results, analyzed the data, and drafted the manuscript.

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Competing interests

The authors declare no competing interests.

Additional information

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