

Molecular-interfacial-electronic triple design for enhanced cooperative adsorption and SERS detection of perfluorooctanoic acid

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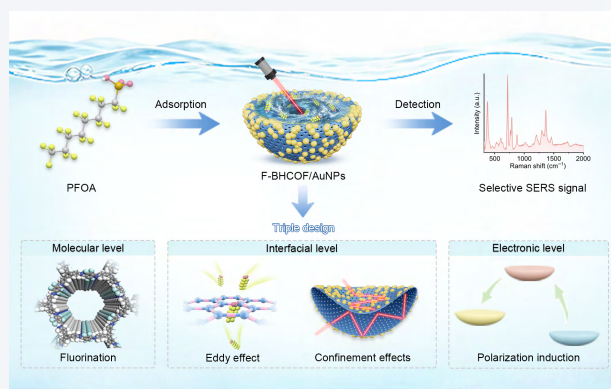
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ABSTRACT: Perfluorooctanoic acid (PFOA), the most environmentally ubiquitous representative of per- and polyfluoroalkyl substances (PFAS), has posed global environmental and health risks due to its persistence. To address the challenges of insufficient adsorption, low intrinsic Raman activity and poor specific recognition of PFOA, this study designed a multifunctional surface-enhanced Raman scattering (SERS) platform based on hollow bowl-like fluorinated covalent organic framework with *in-situ* grown gold nanoparticles (F-BHCOF/AuNPs) at molecular, interfacial and electronic levels. This material was synthesized via an “amorphous-to-crystalline induced transformation” method. First, fluorinated monomers achieve fluorination at the molecular level. Moreover, the controllably synthesized hollow bowl-like structure, at the interfacial level, not only utilizes the “eddy effect” to enhance mass transfer at low concentrations, but also synergistically enhances the electromagnetic field via dual “confinement effects” throughout the structure. Combined with the “polarization induction” mechanism at the electronic level to mediate photoinduced charge transfer, this platform achieves nearly complete adsorption and specific, direct SERS detection of PFOA at environmentally relevant concentrations, with a detection limit of 1.6 ng/L. This platform can be further extended to the rapid screening and exposure risk assessment of PFOA in environmental water samples and daily consumer products including non-stick pan coatings and waterproof outdoor jackets. Furthermore, this work provides a paradigm for the tailored design of functional materials and for overcoming the technical bottleneck of simultaneous adsorption and detection of PFOA and other similar trace-level pollutants with weak response.



KEYWORDS: triple design, eddy effect, bowl-like confinement, polarization induction

1 Introduction

Perfluorooctanoic acid (PFOA) is one of the most human-relevant congeners of per- and polyfluoroalkyl substances (PFAS), a class of globally prevalent persistent environmental pollutants. It has extensive exposure pathways, has been detected in the majority of

serum samples from exposed populations worldwide, and exerts irreversible adverse impacts on the global ecosystem and human health [1–5]. The efficient identification and removal of PFOA from environmental matrices are critical to safeguarding long-term ecological security and preventing public health risks [6–8]. Accordingly, there is an urgent demand for the rational and targeted design of materials that simultaneously achieve adsorption and sensitive detection of PFOA [9–12].

Compared with traditional chromatography and mass spectrometry detection technologies that feature complicated operation and high cost, surface-enhanced Raman scattering (SERS) has emerged as a highly promising approach in the field of PFOA detection by virtue of its inherent advantages including

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rapidity, convenience and high sensitivity [13, 14]. However, there are still prominent challenges hindering its further development. On the one hand, PFOA molecules have a small Raman scattering cross-section, and their insufficient hydrophilicity leads to difficulty in effective binding with existing SERS substrates, which creates a technical bottleneck for direct PFOA detection. On the other hand, the similar Raman spectra of PFAS congeners make it difficult to exert the molecular fingerprinting properties of SERS and achieve direct discrimination between different molecules [15–17]. Meanwhile, this molecular similarity also results in the lack of selective recognition capability of existing substrates and indirect detection technologies. These multiple limitations are particularly pronounced in the detection of low-concentration PFAS. Notably, the key design principles for addressing these limitations are highly consistent with those for the development of high-efficiency PFAS adsorbents [18–21]. In recent years, advanced adsorbent materials for PFAS removal, including porous organic polymers (POPs), metal-organic frameworks (MOFs), and functionalized carbon-based materials, have shown broad application prospects [22–24]. However, the design of such materials has mostly focused on enhancing the adsorption capacity for PFAS, without targeted design and regulation tailored to the occurrence characteristics of PFAS at trace concentrations in real aqueous environments, thus failing to achieve nearly thorough adsorption and stable binding of the target pollutants. Similarly, specific adsorption of target PFAS is still difficult to achieve [25–27]. Therefore, it is essential to realize the synergistic matching of efficient PFOA adsorption and sensitive SERS detection performance.

To address this demand, the key lies in the multi-level oriented design of materials based on the molecular characteristics of PFOA. At the molecular level, rationally guided by established theoretical frameworks for existing PFAS adsorbents [28–30], precision molecular engineering can not only enhance the interfacial affinity and intermolecular interactions with the target analyte to drastically improve adsorption capacity and enrichment efficiency, but also inherently mitigate site competition and signal interference from non-target substances at the source. On this basis, precise regulation of interfacial structures is the core factor that determines the adsorption mass transfer and optical response of the material [31–33]. Rational interfacial design based on morphology dependence can realize synergistic optimization of the two core properties. On one hand, fine regulation of the local flow field can optimize mass transfer behavior, greatly enhance the contact efficiency between target molecules and active sites, and realize rapid adsorption and enrichment of the target at low concentrations. On the other hand, through adaptive design of structure and performance, it can optimize optical impedance matching, enhance the multiple reflection, scattering and optical path confinement effects of incident light, realize significant energy concentration of the light field, and provide a key structural basis for electromagnetic enhancement in SERS systems [34–36]. In SERS detection systems, in addition to the electromagnetic enhancement effect provided by plasmonic materials, structural regulation at the electronic level can be adopted to form a specific photoinduced charge transfer channel between target molecules and substrate materials [37–39]. This specific chemical enhancement dependent on energy level matching is an important way to compensate for the signal of weak Raman-active molecules, and also the core design concept for establishing specific recognition ability of target substances. Therefore, integrating the

above multi-level regulation concepts to design integrated materials with both efficient adsorption and enrichment and specific SERS detection is the core focus of this work.

Herein, we designed a hollow bowl-like fluorinated covalent organic framework (F-COF) with *in-situ* grown gold nanoparticles on the surface (F-BHCOF/AuNPs), which serves as an eddy-assisted SERS platform enhanced by bowl-like confinement and polarization induction. At the molecular level, the use of fluorinated ligands endows F-BHCOF with a highly hydrophobic backbone as well as the preliminary selective screening and adsorption capacity for PFOA. Meanwhile, its open porous structure ensures unhindered access to the adsorption sites within the porous network. Furthermore, at the interfacial level, the “eddy effect” derived from the hollow bowl-like structure endows it with nearly complete and rapid adsorption performance at environmentally relevant concentrations. Moreover, the dual “confinement effects” inside and outside the structure promote the formation of a wide-area electromagnetic enhancement field while effectively suppressing the dissipation of light energy, providing an optimal state for chemical enhancement and ultimately synergistically improving the detection sensitivity. In addition, at the electronic level, an innovative “polarization induction” strategy is adopted, which mediates the amplification of polarizability via photoinduced charge transfer, thus endowing the substrate with the capability of specific recognition of PFOA. Ultimately, the research results demonstrate that, relying on the oriented design at the above three levels, this platform provides a reliable approach for the rapid and nearly thorough adsorption and enrichment of PFOA coupled with highly sensitive and specific SERS detection in real environmental matrices. Meanwhile, this platform also offers a novel solution for the rapid on-site screening of PFOA release and residues in daily high-frequency contact consumer products such as non-stick pans and waterproof outdoor jackets, as well as for the implementation of related exposure risk prevention and control.

2 Experimental

2.1 Synthesis of F-SSCOF, F-SHCOF, F-BHCOF, SSCO, SHCOF, and BHCOF

In a typical synthetic procedure, individual centrifuge tubes were pre-loaded with 1,3,5-tris(4-aminophenyl)benzene (TAPB) (0.04 mmol) and 2,3,5,6-tetrafluoroterephthalaldehyde (TFTA) (0.06 mmol). Subsequently, acetonitrile (ACN, 10 mL) was added to fully dissolve the building blocks, and the resulting solution was thoroughly mixed and stirred at room temperature for 5 min to afford a clear homogeneous solution. Next, acetic acid (HAc) (0.5 mL) was added to initiate the polymerization reaction, and the mixture was vigorously vortexed at room temperature for 6 h. The resulting yellow precipitate was collected by centrifugation and washed three times sequentially with anhydrous ethanol and 1,4-dioxane. The obtained precipitate was re-dispersed in a round-bottom flask charged with a mixed solvent consisting of 1,4-dioxane (5.12 mL), 1,3,5-trimethylbenzene (1.28 mL), ultrapure water (1 mL), and HAc (1.5 mL). The resulting suspension was sealed and aged at 120 °C for 48 h. The obtained red powder was collected by centrifugation and washed repeatedly with copious amounts of tetrahydrofuran. F-BHCOF was finally obtained after drying under vacuum at 80 °C for 6 h. By adjusting the aging temperature to 50 and 100 °C (with all other synthetic parameters

kept constant), solid spherical F-COF (F-SSCOF) and hollow spherical (F-SHCOF) were obtained as yellow and orange powders, respectively. In addition, by replacing the TFTA monomer with terephthalaldehyde (TPA) (0.06 mmol), solid spherical COF (SSCOF), hollow spherical COF (SHCOF), and hollow bowl-like COF (BHCOF) powders were obtained following the exact same synthetic procedure at aging temperatures of 50, 100, and 120 °C, respectively.

2.2 Synthesis of F-SHCOF/AuNPs and F-BHCOF/AuNPs

AuNPs were grown *in-situ* on the surface of fluorinated covalent F-COF materials via an *in-situ* reduction method. For the typical preparation of F-BHCOF/AuNPs, the as-prepared F-BHCOF was added into 10 mL of ultrapure water and stirred thoroughly. Subsequently, sodium borohydride (NaBH_4) (500 μL , 0.1 M) was added dropwise under ice bath conditions, and the mixture was stirred for 2 h followed by storage at 4 °C overnight. The resultant product was collected by centrifugation and washed three times with ultrapure water. F-BHCOF/AuNPs was finally obtained after drying under vacuum at 80 °C for 12 h. F-SHCOF/AuNPs was prepared following the exact same synthetic procedure by substituting F-BHCOF with F-SHCOF.

2.3 Real sample analysis

To assess the practical application potential of the as-prepared SERS platform in real-life scenarios, the following real sample tests and analysis were performed. First, for the spiking test of commercial drinking water, PFOA powder was dissolved in commercial drinking water to prepare spiked solutions at three concentration levels (10, 100, and 1000 ng/L), and the detection performance of the platform was evaluated via the standard spiked recovery method. Subsequently, a non-stick pan was treated to simulate the actual daily household use process. Abrasion tests were carried out using three cleaning tools with different hardness, namely soft cloth, scouring pad, and steel wool ball. One brushing cycle was defined as a single unidirectional wipe over the entire surface of the pan bottom. Four groups of abrasion tests with different intensities were performed, with 10, 100, 500, and 1000 brushing cycles set for each group respectively.

Prior to each test, 100 mL of ultrapure water was added into the non-stick pan, heated to boiling and maintained for 10 min, then cooled to room temperature. The liquid in the pan was collected and analyzed using the integrated device prepared in this study. For the measurement of textile samples, fabric fragments with the size of 5 mm $\times$ 5 mm were cut from multiple random sites of each sample, then fabric pieces with a total area of 1 cm² were randomly selected, immersed in 1 mL methanol and ultrasonicated for 40 min. The 0.5 mL extracts were dried using a nitrogen evaporator, reconstituted with 1 mL of ultrapure water, and then analyzed with the integrated device developed in this work.

2.4 Other experimental procedures

The rest of experimental sections including necessary reagents, apparatuses, PFOA adsorption experiments, kinetic adsorption studies, isotherm adsorption studies, Raman measurement, absorption energy calculation, molecular energy level calculation, finite-difference time-domain (FDTD) simulation, and COMSOL simulation for this study are detailed in the Electronic Supplementary Material (ESM).

3 Results and discussion

3.1 Synthesis and characterization of materials

In this study, fluorinated solid COFs (F-SCOFs) and fluorinated hollow COFs (F-HCOFs) nanoparticles with uniform size, high crystallinity and diverse morphologies were first prepared via regulation at both molecular and interfacial levels, using fluorinated monomers and an “amorphous-to-crystalline induced transformation” synthetic method. This method consists of two steps, in which amorphous covalent organic polymers are first formed from monomers, followed by induced high-temperature crystallization. Specifically, TAPB and the fluorinated monomer TFTA were dissolved in acetonitrile and mixed by stirring at room temperature, followed by the addition of HAc to initiate the polymerization reaction and obtain polymer precipitates. Subsequently, a mixed solution of water, acetic acid, mesitylene and 1,4-dioxane was used as the crystallization inducer, and the dynamic imine exchange reaction was initiated under heating to achieve the transformation to crystalline structure (Fig. 1(a)). During this process, the temperature effectively regulated the shift of the dynamic equilibrium between surface crystallization and internal hydrolysis, thus enabling the controllable structural evolution. Accordingly, by setting the reaction temperature at 50, 100, and 120 °C respectively, F-SSCOF (Fig. 1(b)(i) and Fig. S1(a) in the ESM), F-SHCOF (Fig. 1(b)(ii) and Fig. S1(b) in the ESM) and F-BHCOF (Figs. 1(b)(iii) and 1(b)(iv), and Fig. S1(c) in the ESM) were obtained sequentially. This is supported by the temperature-dependent structural evolution. At the low temperature of 50 °C, only surface crystallization occurred. At 100 °C, preferential surface crystallization and internal dissolution took place, resulting in the formation of spherical cavities. At 120 °C, as the shell thickness decreased further, capillary forces caused the collapse of the shell and the formation of bowl-shaped cavities. Using the same method, we performed the identical synthesis procedure with the combination of TAPB and the non-fluorinated monomer TPA, and obtained non-fluorinated COFs with similar morphologies, namely SSCO, SHCO and BHCO (Figs. S2(a)–S2(f) in the ESM). Notably, as observed from scanning electron microscopy (SEM) and transmission electron microscopy (TEM), the F-COFs exhibited rough wrinkles on the surface compared with the non-fluorinated COFs, which is mainly attributed to the repulsion between strongly electronegative fluorine atoms within the layers.

The crystallinity of the as-synthesized F-COFs was analyzed by powder X-ray diffraction (PXRD), where F-SSCOF, F-SHCOF and F-BHCOF all exhibit a sharp diffraction peak at 2.9° (Fig. 1(c)) matching well with the simulated diffraction patterns, and the peak intensity increases with rising synthesis temperature, indicating improved crystallinity. Meanwhile, their specific surface areas were calculated from the nitrogen adsorption–desorption data collected at 77 K, and the pore size distributions were further calculated via non-local density functional theory (NLDFT) on this basis. As shown in Fig. 1(d) and Figs. S3(a)–S3(c) in the ESM, F-SSCOF, F-SHCOF, and F-BHCOF possess identical micropore distributions ($\text{Dp}_1 = \text{Dp}_2 = \text{Dp}_3 = 1.4 \text{ nm}$). Compared with F-SSCOF ($\text{BET}_1 = 256 \text{ m}^2/\text{g}$), elevated synthesis temperature leads to a significant increase in the specific surface areas of F-SHCOF and F-BHCOF, while the specific surface area of F-BHCOF shows a slight decrease primarily attributed to the folding of the bowl-like edges ($\text{BET}_2 = 521 \text{ m}^2/\text{g}$, $\text{BET}_3 = 494 \text{ m}^2/\text{g}$), which also verifies the substantial

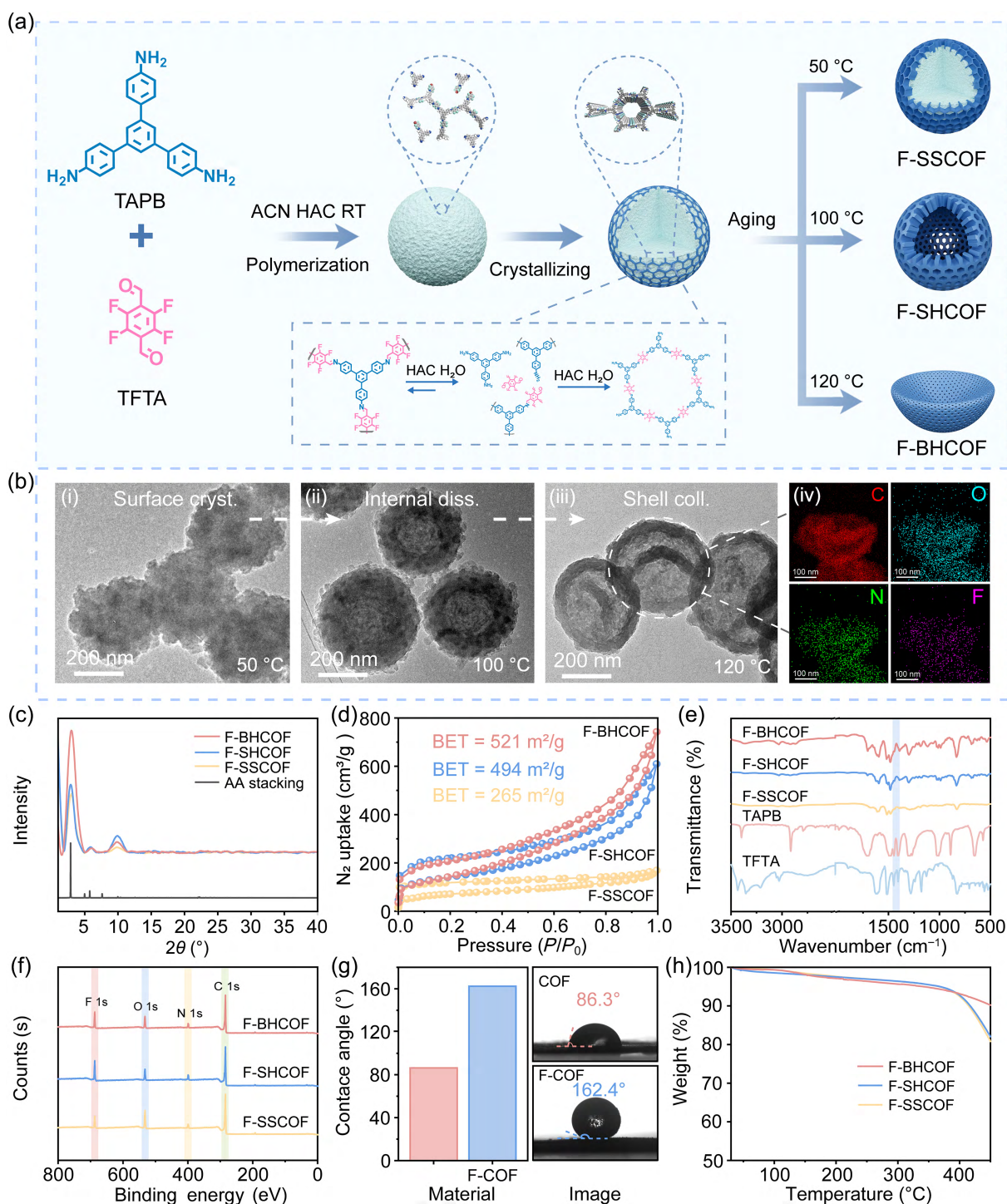


Figure 1 (a) Schematic illustration of the formation process for F-SSCOF, F-SHCOF, F-BHCOF. (b) Temperature-dependent TEM and energy dispersive spectroscopy (EDS) images for understanding the formation of (i) F-SSCOF, (ii) F-SHCOF, and (iii) F-BHCOF. (c) PXRD patterns of F-BHCOF, F-SHCOF, F-SSCOF, and AA stacking. (d) Brunauer–Emmett–Teller (BET) curves of F-BHCOF, F-SHCOF, and F-SSCOF. (e) FT-IR spectra of F-BHCOF, F-SHCOF, F-SSCOF, TAPB, and TFTA. (f) XPS curves of F-BHCOF, F-SHCOF, and F-SSCOF. (g) Contact angle of COF and F-COF. (h) TGA curves of F-BHCOF, F-SHCOF, and F-SSCOF.

evolution process of crystallization. The Fourier transform infrared (FT-IR) spectra of F-COFs showed the characteristic peak of the imine structure at 1607 cm⁻¹, while the N–H stretching vibration peaks of TAPB at 3430 and 3354 cm⁻¹, as well as the aldehyde C–H stretching vibration peaks of TFTA at 2852 and 2787 cm⁻¹, all disappeared (Fig. 1(e)), confirming the successful synthesis of these materials. Meanwhile, X-ray photoelectron spectroscopy (XPS)

further confirmed the successful construction of the framework and the successful introduction of fluorinated functional groups via the detection of characteristic C, N, O, and F elements (Fig. 1(f)). The synthesis of SSCO, SHCO, and BHCO also exhibited the same trend (Figs. S4(a)–S4(c) in the ESM). This fluorination also significantly enhanced the hydrophobicity of the materials, with the contact angle increasing from 86.3° to 162.4° (Fig. 1(g)),

constructing an intrinsic strong hydrophobic interface of the materials. In addition, thermogravimetric analysis (TGA) curves showed the good thermal stability of F-SSCOF, F-SHCOF, and F-BHCOF, with only negligible mass loss below 350 °C and well-maintained structural integrity (Fig. 1(h)).

3.2 PFOA adsorption experiments and mechanism

Adsorption studies were performed to evaluate the PFOA adsorption efficiency from water of these as-prepared COFs and F-COFs. Unless otherwise specified, all adsorption experiments were carried out using homogeneous adsorbent dispersions at room temperature of 25 °C. The PFOA concentration in all experiments was determined by liquid chromatography-tandem mass

spectrometry (LC-MS/MS), and the adsorption efficiency was calculated according to Eqs. (S1)–(S10) in the ESM, with further details elaborated in the Methods section in the ESM. First, adsorption performance studies were conducted at an identical PFOA concentration of 0.2 mg/L. The results showed that the adsorption performance of F-COFs was significantly improved compared with that of non-fluorinated COFs after sufficient adsorption equilibrium was reached (Fig. 2(a)). This is attributable to our molecular level design, wherein the F-F interactions between the F functional groups introduced by the fluorinated monomers and the PFOA molecules further enhance intermolecular affinity. As shown by the results of the intermolecular force simulations and adsorption energy calculations for COF and F-COF toward PFOA

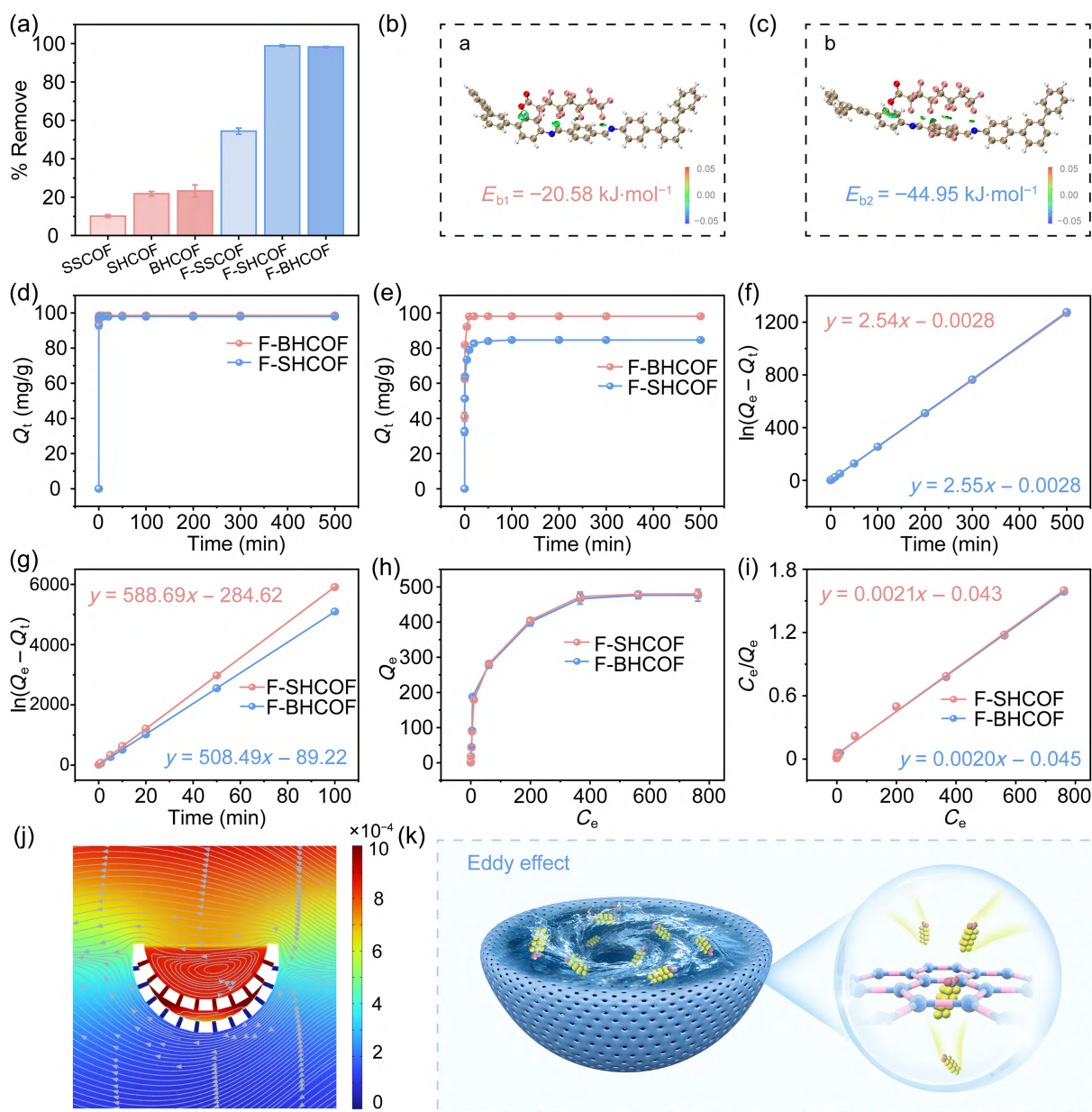


Figure 2 (a) Adsorption efficiencies to PFOA with SS COF, SH COF, BH COF, F-SS COF, F-SH COF, and F-BH COF. Molecular interactions and binding energy between PFOA and (b) COF and (c) F-COF. Adsorption kinetics curve of F-BHCOF and F-SHCOF for (d) high and (e) low concentrations of PFOA. Adsorption kinetics with pseudo-second-order fitting for (f) high and (g) low concentrations of PFOA by F-SHCOF and F-BHCOF. (h) Adsorption isotherm of PFOA onto F-SHCOF and F-BHCOF. (i) Adsorption isotherm data fitted to the Langmuir model for F-SHCOF and F-BHCOF. (j) COMSOL multiphysics modeling of PFOA adsorption into F-BHCOF. (k) Schematic diagram of F-BHCOF eddy-assisted adsorption of PFOA.

(Figs. 2(b) and 2(c)), this modification results in an adsorption energy significantly higher than that of non-fluorinated COF ($|E_{b1}| = 20.58 \text{ kJ/mol} < |E_{b2}| = 44.95 \text{ kJ/mol}$). This, combined with the material's intrinsic hydrophobic framework and high specific surface area, collectively provides the fundamental performance guarantee for PFOA adsorption.

In addition, HCOFs exhibited remarkably higher adsorption performance than SCOFs. Among them, both F-SHCOF and F-BHCOF achieved a PFOA adsorption rate of over 99% in water, indicating their excellent application potential (Fig. 2(a)). To further evaluate the difference in adsorption efficiency between the two materials, detailed kinetic adsorption studies were performed. As shown in Fig. 2(d), at the above high PFOA concentration, both materials exhibited ultrafast adsorption kinetics. Nearly complete adsorption was achieved within the few seconds required for sampling and filtration, and no desorption occurred throughout the process. However, at environmentally relevant PFOA concentration of $1 \mu\text{g/L}$, the two materials exhibited significant differences in adsorption performance. Even at this trace concentration, nearly 80% of PFOA was adsorbed by F-BHCOF within 1 min. Adsorption equilibrium was reached within 10 min with almost complete PFOA adsorption, which was far superior to the performance of F-SHCOF (Fig. 2(e)). The kinetic data were then fitted with pseudo-first-order and pseudo-second-order kinetic models. As expected, the experimental data exhibited a better fit with the pseudo-second-order model, which indicates that the adsorption of PFOA by both F-SHCOF and F-BHCOF under high and low concentration conditions is dominated by chemisorption (Figs. 2(f) and 2(g), and Figs. S5(a) and S5(b) in the ESM). Among them, the apparent rate constants of F-BHCOF are $2321 \text{ g/(mg}\cdot\text{min)}$ at high concentration and $3951 \text{ g/(mg}\cdot\text{min)}$ at low concentration (Table S1 in the ESM). Notably, the adsorption kinetic performance of F-BHCOF, especially at low concentration, far outperforms the reported PFOA adsorption cases in the literature (Table S2 in the ESM). In addition, to evaluate the maximum adsorption capacity of F-SHCOF and F-BHCOF, the adsorption isotherms of the two materials were plotted with initial PFOA concentrations ranging from 0.2 to 1000 mg/L . The results in Fig. 2(h) show that the maximum adsorption capacities of F-SHCOF and F-BHCOF are comparable ($Q_{m1} = 495.1 \text{ mg/g}$, $Q_{m2} = 487.8 \text{ mg/g}$), and the Langmuir model presents a higher correlation coefficient for both materials ($R_1^2: 0.9978 > 0.9590$, $R_2^2: 0.9975 > 0.9450$) (Fig. 2(i), and Fig. S6(a) and Table S3 in the ESM). This is attributed to the ordered pore channels of HCOFs, which are radial pores extending from the center to the surface and are highly favorable for the loading and diffusion of guest molecules.

Therefore, the key factor responsible for this difference in adsorption performance lies in the regulation effect of the material's interfacial structure on mass transfer. To clarify this mechanism, we constructed 2D models of three structures (F-SSCOF, F-SHCOF, and F-BHCOF) to visualize the influence of COF interface on the adsorption process. The simulation setup is shown in Figs. S7(a) and S7(b) in the ESM and Fig. 2(j), where all surface models were set as adsorption sites. According to the simulation results, on the one hand, the stable hydrophobic microdomains provided by the hydrophobic cavities reduce the interfacial energy barrier for PFOA migration from the aqueous phase to the adsorbent surface. Meanwhile, the presence of cavities provides additional diffusion pathways and reduces mass transfer resistance. This thermodynamically drives the preferential enrichment of PFOA in

the cavities, while the shorter diffusion pathways avoid the rapid loss of adsorption capacity caused by surface adsorption saturation. On the other hand, the hollow bowl-like structure possesses superior hydrodynamic properties compared with the hollow spherical structure. The unique bowl-like curved surface can induce a surface "eddy effect" and form local fluid circulation, which not only accelerates the migration rate of PFOA molecules in water to the adsorbent surface and internal cavities, but also inhibits the desorption of adsorbed PFOA, thus significantly enhancing the local concentration enrichment of PFOA. This is the core mechanism for the significantly better adsorption performance of F-BHCOF than F-SHCOF at low concentrations (Fig. 2(k)). Based on the above comprehensive analysis, F-BHCOF is a structure with more prominent advantages and higher application potential. The rapid and excellent adsorption kinetics for low-concentration PFOA achieved by F-BHCOF is not only conducive to integration with portable detection methods, but also can more faithfully reflect the actual concentration of PFOA in aqueous solution, thus improving the accuracy and sensitivity of detection.

3.3 Construction of F-BHCOF/AuNPs SERS sensing platform via *in-situ* reduction method

Based on the strong PFOA adsorption capacity of F-BHCOF, we further modulated its electronic level by immobilizing AuNPs onto the material surface, to develop a dual-functional nanoreactor (F-BHCOF/AuNPs) integrating high-efficiency PFOA adsorption and SERS detection. Au^{3+} ions first coordinated with the imine groups in the sample, then the chelated Au^{3+} ions were reduced under the action of NaBH_4 to induce the formation of ultrasmall-sized AuNPs (Fig. 3(a)). TEM images and corresponding EDS elemental mapping (Figs. 3(b) and 3(c)) confirmed that ultrasmall-sized AuNPs (5 nm) were uniformly grown on the surface of F-BHCOF. The phase composition of the as-synthesized F-BHCOF was characterized by XRD. As shown in Fig. 3(d), the intrinsic characteristic diffraction peaks of F-BHCOF were well retained, and an additional characteristic peak at 38.5° corresponding to the (111) crystal plane of AuNPs appeared, which confirmed the successful introduction of AuNPs without destroying the original crystalline structure of the material. In addition, consistent analytical results were obtained via XPS and FTIR (Figs. S8(a) and S8(b) in the ESM).

We further investigated the physicochemical properties of this material. BET test analysis (Fig. 3(e)) showed that the introduction of AuNPs had almost no impact on the specific surface area of F-BHCOF ($\text{BET}_4 = 485 \text{ m}^2/\text{g}$), with only a slight decrease induced by the mass effect, and no pore blockage was observed (Fig. S9 in the ESM). Water contact angle test (inset of Fig. 3(e)) showed that the material surface still retained a superhydrophobic interface ($\text{Dp4} = 119.6^\circ$) after AuNPs loading. The results of adsorption experiments confirmed that this modification had no adverse effect on the adsorption performance of the material (Fig. 3(f)), which is attributed to the effective compensation for adsorption performance via the improved aqueous dispersibility of the material.

On this basis, we further systematically investigated the SERS detection performance of F-BHCOF/AuNPs toward PFOA. One of the most critical challenges for using COF materials as SERS substrates is that their intrinsic photoluminescence (PL) background severely hinders the detection of target molecules [36]. Therefore, we first investigated the optimal excitation light for SERS

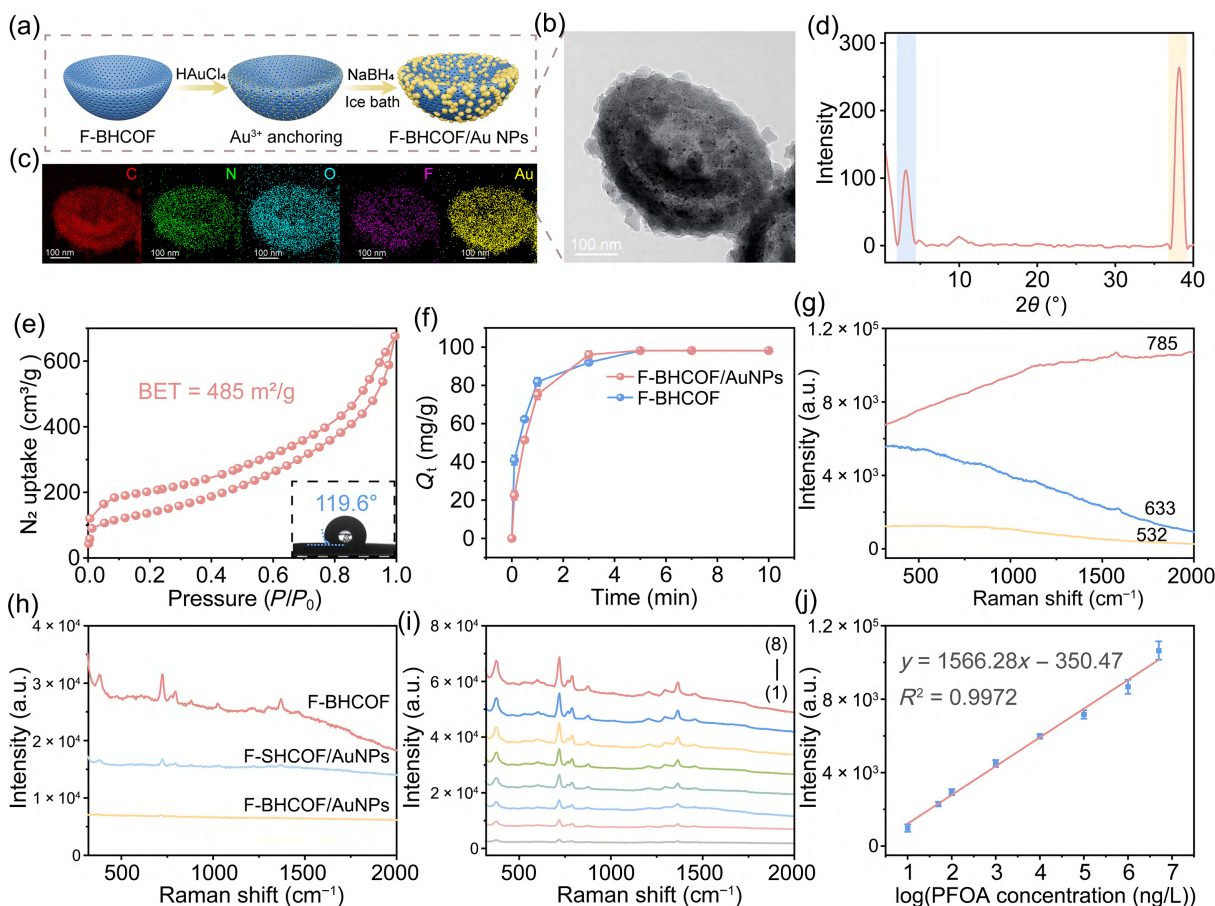


Figure 3 (a) Schematic illustration of the formation process for F-BHCOF/AuNPs. (b) TEM and (c) EDS image of F-BHCOF/AuNPs. (d) PXRD patterns of F-BHCOF/AuNPs. (e) BET curves and contact angle angle of F-BHCOF/AuNPs. (f) Adsorption kinetics curve of F-BHCOF/AuNPs and F-BHCOF. (g) SERS spectrum of COF at a laser wavelength of 785, 633, and 532. (h) SERS spectra of PFOA on the F-BHCOF, F-SHCOF/AuNPs, and F-BHCOF/AuNPs. (i) SERS spectra of PFOA at various concentrations on the F-BHCOF/-AuNPs substrate: (1) 10, (2) 50, (3) 100, (4) 10^3 , (5) 10^4 , (6) 10^5 , (7) 10^6 , and (8) 5×10^6 ng/L. (j) Linear relationship between intensity and logarithm of PFOA concentration.

measurements. As shown in Fig. 3(g), a strong PL background was observed when excitation wavelengths of 532 and 633 nm were applied, which severely reduces the ratio of the molecular SERS signal to the total signal intensity. Accordingly, a 785 nm laser, which induced negligible background interference from the F-BHCOF/AuNPs substrate, was selected as the SERS light source for subsequent detection experiments. We further investigated the SERS detection sensitivity of F-BHCOF, F-SHCOF/AuNPs (Figs. S10(a)–S10(d) in the ESM) and F-BHCOF/AuNPs toward PFOA at the identical concentration of 1 $\mu\text{g/L}$. As shown in Fig. 3(h), no characteristic peak of PFOA was detected for F-BHCOF without AuNPs modification. While the characteristic peak of the C–F bond of PFOA at 719 cm^{-1} was observed for both F-SHCOF/AuNPs and F-BHCOF/AuNPs, the latter exhibited much higher enhancement ability and sensitivity toward PFOA. This fully demonstrates the necessity of regulation at both the interfacial and electronic levels for the improvement of detection performance. Therefore, the detection performance of F-BHCOF/AuNPs toward PFOA with gradient concentrations was investigated under optimal conditions (Fig. 3(i)). In the range of 10 to 5×10^6 ng/L, the SERS peak intensity at 719 cm^{-1} showed a good linear relationship with the logarithm of PFOA concentration (Fig. 3(j)), with a linear equation of $y = 1566.28x - 350.47$ and a correlation coefficient R^2 of 0.9972. The limit of detection (LOD) was calculated to be 1.6 ng/L

($\text{LOD} = 3\sigma/k$, where σ is the standard deviation of blank baseline signal and k is the slope of calibration curve), which is lower than the latest standard of 4.0 ng/L issued by the U.S. Environmental Protection Agency (EPA) in 2024. This result demonstrates performance advantages comparable to recently reported detection strategies, as well as great application potential for the detection of low-concentration PFOA in environmental matrices (Table S4 in the ESM).

Based on the sensitive detection capability of F-BHCOF/AuNPs toward PFOA, we further applied it to the detection of PFOA analogs. Figure 4(a) shows the structural formulas of perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorooctane sulfonic acid (PFOS), perfluorononanoic acid (PFNA), and perfluorodecanoic acid (PFDA), which exhibit highly similar structures. And their physicochemical properties are also similar due to their highly fluorinated backbones.

Figure 4(b) shows the SERS spectra of these six substances at high concentration, which present high similarity. However, on the basis of the sufficient detection sensitivity endowed to the material by interfacial regulation, combined with principal component analysis (PCA), a dimensionality reduction algorithm in machine learning, the discrimination ability toward these analogs can be significantly enhanced. As shown in Fig. 4(c), these six substances

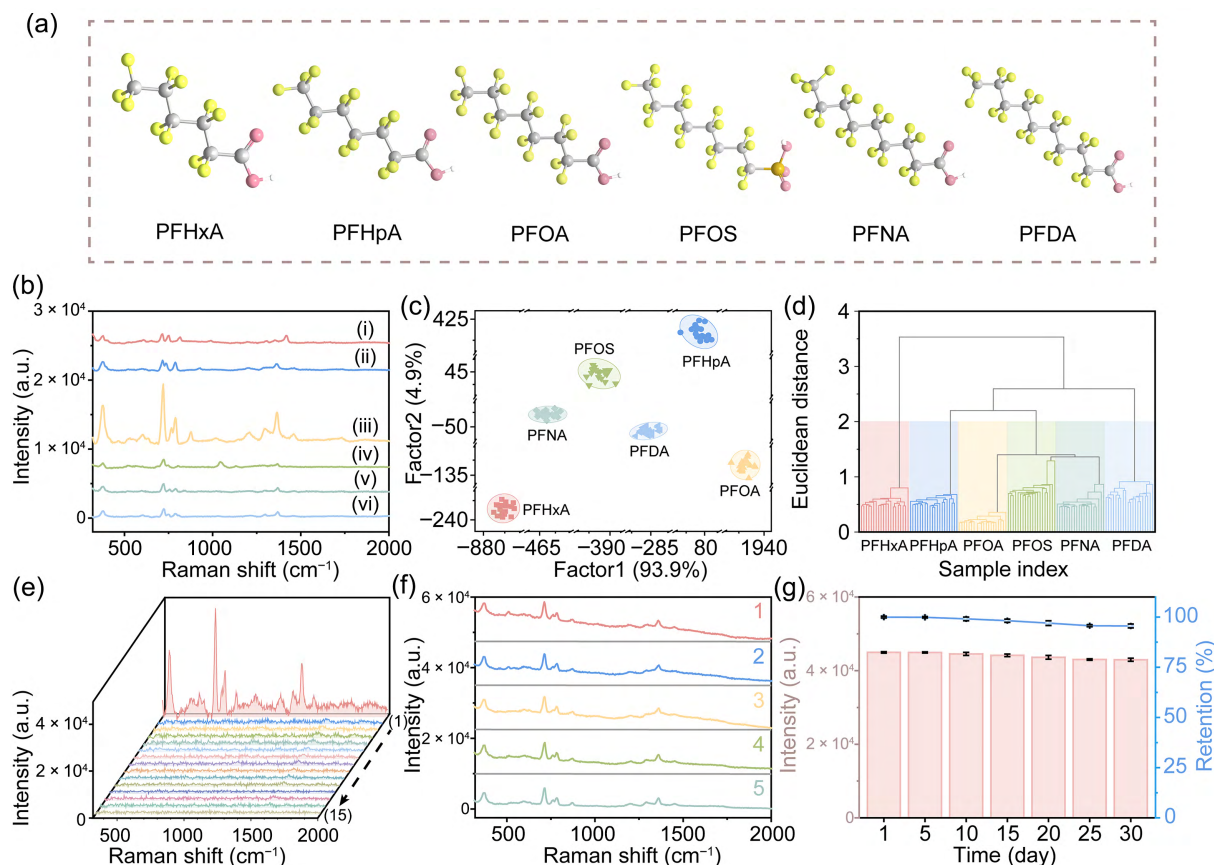


Figure 4 (a) Structural formulas and (b) SERS spectra of (i) PFHxA, (ii) PFHpA, (iii) PFOA, (iv) PFOS, (v) PFNA, and (vi) PFDA at 1 $\mu\text{g/L}$. (c) The PCA score plot and (d) HCA dendrogram. (e) SERS spectra of (1) PFOA, (2) PFHxA, (3) PFHpA, (4) PFOS, (5) PFNA, (6) PFDA, (7) propionic acid, (8) caprylic acid, (9) benzoic acid, (10) NaCl, (11) Na_2SO_4 , (12) trifluoroacetic acid, (13) perfluorobutanoic acid, (14) Cu^{2+} , and (15) Pb^{2+} at 1 $\mu\text{g/L}$. (f) The reproducibility in the different batch. (g) The storage stability examined every 5 days for 30 days.

can be clearly distinguished, which verifies the application potential of F-BHCOF/AuNPs in the identification of PFOA and its analogous PFAS. Figures S11(a) and S11(b) in the ESM show the loading plots of PC1 and PC2. Multiple spectral peaks in the range of 400 to 2000 cm^{-1} present high discrimination coefficients, indicating that the effective discrimination of these PFAS is achieved through the synergistic contribution of multiple key SERS characteristic peaks. In addition, hierarchical cluster analysis (HCA) based on the K-means classification method was performed according to the clustering characteristics of these SERS spectra. As shown in Fig. 4(d), the horizontal branches in the dendrogram represent the association between samples and categories, while the vertical branches represent the distance between categories. The HCA results show six distinct clusters corresponding to the above six PFAS respectively, which accurately distinguish the subtle differences in the SERS spectra and demonstrate the application prospect of F-BHCOF/AuNPs in the species identification of PFAS.

Interestingly, F-BHCOF/AuNPs exhibited remarkable selectivity toward PFOA molecules at low concentrations. Control experiments were performed to evaluate the sensing capability of F-BHCOF/AuNPs toward the above fluorinated acids with homologous structures at environmentally relevant concentrations (Figs. 4(e)(1)–4(e)(6)) and other non-fluorinated strong acids, including propionic acid, octanoic acid and benzoic acid (Figs. 4(e)(7)–4(e)(9)). No obvious characteristic peaks were observed in the SERS spectra of these interfering substances after

detection. This result demonstrates the successful construction of an intrinsic PFOA specific electron transfer channel within the material via electronic level modulation. Considering that common pollutants such as NaCl, Na_2SO_4 , Pb^{2+} , and Cu^{2+} may also exist in contaminated water, selectivity tests were also performed on these substances both individually and as a mixed solution, and no obvious SERS signal was detected in either case (Figs. 4(e)(10)–4(e)(15), Fig. S12 in the ESM). In addition, reproducibility and long-term stability are critical evaluation indicators for SERS substrates. Five batches of F-BHCOF/AuNPs substrates were prepared separately to test five PFOA samples with the same concentration. The results are shown in Fig. 4(f), with a relative standard deviation (RSD) of 1.45%, indicating excellent reproducibility. Subsequently, PFOA detection was performed using the same batch of F-BHCOF/AuNPs at different time points within 30 days of storage at room temperature (Fig. 4(g)). The signal intensity only decreased by 4.43%, which confirmed its applicability in practical sensing scenarios.

3.4 Elucidation of detection mechanism

To further elucidate the highly sensitive and selective sensing mechanism of F-BHCOF/AuNPs toward PFOA, we performed a series of simulations and theoretical calculations. As shown in Fig. S13 in the ESM, the complex refractive index (n) of F-BHCOF at 785 nm is 1.466, with an imaginary part (k) of 0.02. Accordingly, the corresponding dielectric constants were calculated using the

equations $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$, with the results of $\varepsilon_1 = 2.149$ and $\varepsilon_2 = 0.005864$. Based on the above values, we investigated the local electromagnetic field distribution from both internal and external aspects of the interface via the finite element method (FEM), and analyzed the electromagnetic enhancement and chemical enhancement of SERS combined with photon propagation behavior. The wavelength of the incident laser in the simulation was set to 785 nm. The morphology and size of F-BHCOF/AuNPs and F-SHCOF/AuNPs were set with reference to TEM characterization data to match the actual material structure. For the external structure, the curved geometry of the bowl-like architecture acts as a high-efficiency optical concentrator (Figs. 5(a) and 5(b)). Light undergoes multiple refraction and reflection on the concave surface, which excites and enhances the localized surface plasmon resonance (LSPR) of AuNPs. While enhancing the effect of hot spots, this process enables the formation of a wide-area electromagnetic enhancement field extending deep into the inner cavity. For the internal structure, after entering the hollow interior, light undergoes multiple scattering and refraction in the confined space. Compared with the spherical cavity (Figs. 5(c) and 5(d)), light propagation in the bowl-like inner cavity is more intensive and complex, which can effectively suppress the rapid dissipation of light energy. This greatly extends the effective propagation path of photons, which not only increases the interaction time and probability between photons and PFOA in the inner cavity, but also provides optimal conditions for interfacial charge transfer. This process promotes the electron transition of adsorbed PFOA, thus

significantly enhancing the molecular polarizability. This process directly contributes to the chemical enhancement mechanism, which synergizes with the external-dominated electromagnetic enhancement mentioned above to greatly improve the detection capability for trace amounts of PFOA.

To further investigate the selective mechanism of F-BHCOF/AuNPs toward PFOA at the electronic level, we analyzed the energy level structures of the material and target molecule. According to the Lombardi model, the SERS charge transfer (CT) resonance intensity follows the relation $\text{ICT} \propto 1/[(E_{\text{Laser}} - \Delta\text{ECT})^2 + \Gamma^2]$, where E_{Laser} denotes the excitation laser energy, ΔECT represents the CT energy gap between the material and the target molecule, and Γ refers to the full width at half maximum of the spectral peak. When the laser energy is precisely matched with the charge-transfer energy gap, electrons can transfer from the highest occupied molecular orbital (HOMO) of the molecule to the conduction band (CB) of the material, or from the valence band (VB) of the material to the lowest unoccupied molecular orbital (LUMO) of the molecule. This CT resonance effect serves as the core for realizing highly selective detection of PFOA [40]. The band gap of F-BHCOF was calculated to be 2.03 eV via UV-vis diffuse reflectance spectroscopy (UV-vis DRS) (Fig. 5(e) and Fig. S14(a) in the ESM) and ultraviolet photoelectron spectroscopy (UPS) (Fig. 5(f) and Fig. S14(b) in the ESM), with its VB and CB determined to be -6.89 and -4.86 eV, respectively. Relevant calculation details are provided in Text S1 in the ESM. The HOMO and LUMO energy levels of PFOA and its analogs were calculated

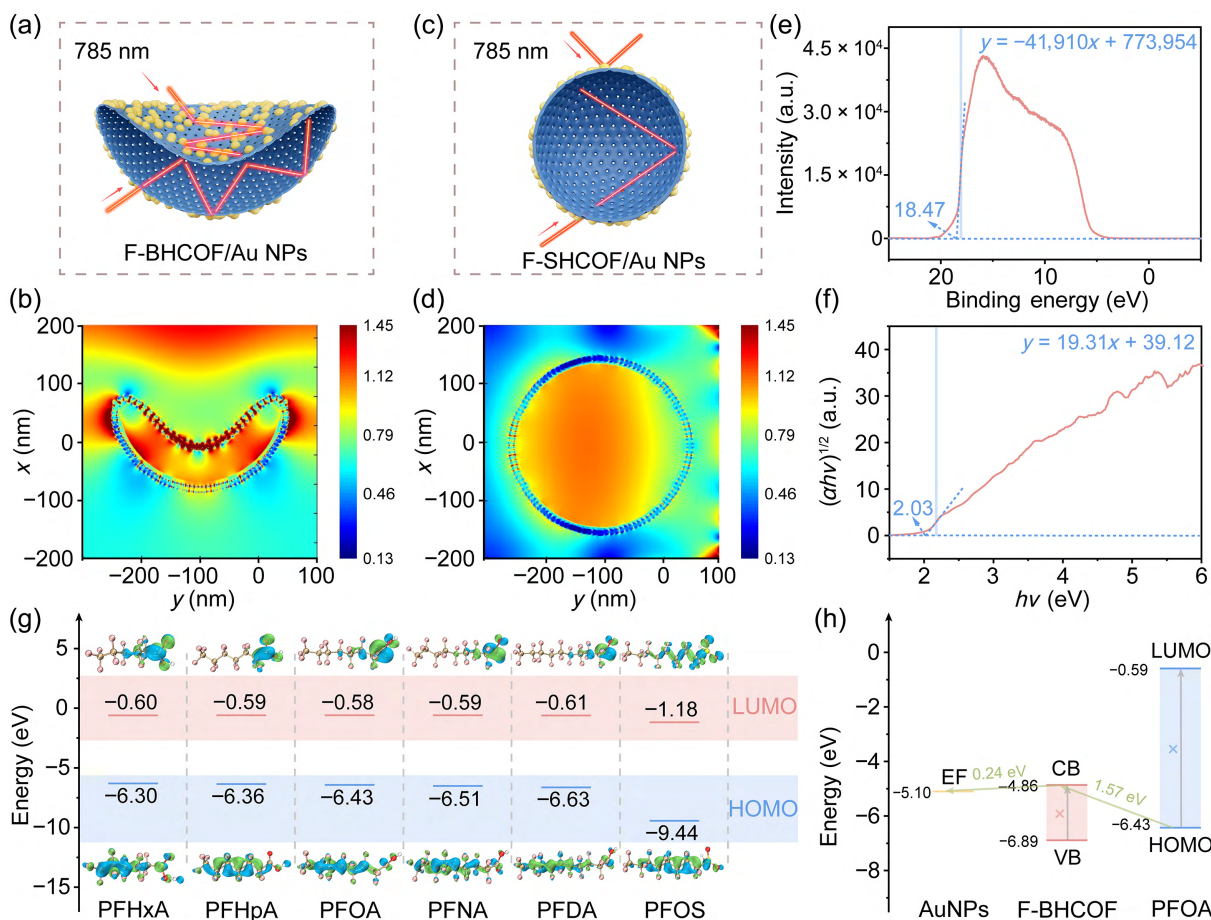


Figure 5 The external and internal electric field distributions of ((a) and (b)) F-BHCOF/AuNPs and ((c) and (d)) F-SHCOF/AuNPs at wavelengths of 785 nm. (e) UPS spectra and (f) band gaps of F-BHCOF. (g) HOMO and LUMO orbitals and electron cloud diagram. (h) Energy level diagram and electron transition mechanism.

via density functional theory (DFT), with the B3LYP functional and Def2-T2VP basis set adopted for the specific calculations. The corresponding electron cloud distributions are shown in Fig. 5(g). Based on the above energy level structures, the selective chemical enhancement mechanism can be clearly elucidated (Fig. 5(h)). Calculations show that the energy level difference between the HOMO of PFOA molecules and the CB of the COF is 1.57 eV, which is highly consistent with the photon energy of the 785 nm SERS laser (1.58 eV). This satisfies the resonance condition and thus efficiently triggers the photoinduced charge transfer (PCT) mechanism. For interfering substances including PFOS, PFNA and PFDA, the energy of the 785 nm laser is too low to excite the electron transition from their HOMO orbitals. For PFHxA and PFHpA with shorter chain lengths, the energy cannot be matched due to the difference in energy levels, which also fails to satisfy the PCT condition. This process is the core of the selective chemical enhancement effect. Furthermore, the electrons excited to F-BHCOF can be rapidly transferred to the AuNPs grown on the outer surface, which ensures the effective separation of photogenerated charges and thus sustains the amplification of PFOA molecular polarizability. In addition, since the band gap of F-BHCOF is 2.03 eV, which is much higher than the energy of the 785 nm laser, the light source is insufficient to excite the transition of intrinsic electrons of F-BHCOF itself, thus presenting extremely low PL background interference in the SERS spectra. In contrast, the application of 532 and 633 nm lasers induces strong PL background interference. For other substances including Na_2SO_4 , they cannot be effectively adsorbed by F-BHCOF/AuNPs due to the lack of hydrophobicity and F-F interactions, so no interfering response is observed during detection.

3.5 Device setup and real sample detection

To further verify the PFOA treatment performance of F-BHCOF/AuNPs in real samples, we constructed a portable water treatment device, as shown in Fig. 6(a), and Figs. S15(a) and S15(b) in the ESM. The device consists of a syringe and a syringe-driven filter column, which is equipped with a hydrophobic filter membrane connected to the syringe plunger and a hydrophilic filter membrane fixed at the outlet. The presence of the filter membranes ensures the permeation process, enables sufficient contact between the sample and F-BHCOF/AuNPs, and prevents leakage caused by unnecessary diffusion. 0.5 mg of F-BHCOF/AuNPs was filled between the two filter membranes in the filter column, and the obtained device can achieve efficient adsorption of PFOA in water through a simple injection-filtration process. Subsequently, the filter column can be opened for direct *in-situ* SERS detection of PFOA.

Performance verification of the device was conducted with PFOA at an environmentally relevant concentration of 1 $\mu\text{g/L}$ as the target analyte, and the detection results were highly consistent with the linear response. Meanwhile, Raman mapping imaging showed that the intensity of the PFOA characteristic peak was highly uniform in the detection area, with no obvious signal aggregation or blank regions (Fig. 6(b)), which verified the reliability and spatial consistency of the device. In addition, five cycling experiments were performed via direct methanol desorption by suction (Fig. 6(c)), which confirmed the operational stability and reusability of the device.

To further verify the applicability of the device in practical application scenarios, four types of real water and environmental samples, including commercial purified drinking water, Lake Lihu

water, as well as soil and algae samples collected from Lake Lihu, were selected for detection in this study (Fig. 6(d)). The results demonstrated that no characteristic PFOA signal was detected in any of the tested samples. To evaluate the accuracy of the device, gradient spike experiments at 10, 100, and 1000 ng/L were performed on commercial drinking water (Fig. 6(e)), with recoveries ranging from 92.30% to 107.15% (Table S5 in the ESM).

Meanwhile, targeting the potential migration scenarios of PFOA in daily life, simulation experiments were carried out on non-stick pans using PFOA as a processing aid (Fig. 6(f)). In the experiments, three cleaning tools with different hardness, including soft cloth, scouring pad and steel wool ball, were used for 10, 100, 500, and 1000 scrubbing cycles to simulate the long-term use process. Liquid samples were collected after 10, 100, 500, and 1000 brushing cycles, followed by boiling and cooling, then processed and detected using the above-mentioned device. The results showed that even under the long-term use condition simulated by high-frequency scrubbing with soft cloth and scouring pad, slow release of 3–6 ng/L PFOA from the shallow layer of the coating could still be observed (Fig. 6(g)). The steel wool ball with higher hardness caused obvious scratches on the coating, leading to a massive release of PFOA at approximately 7000 ng/L. Although global regulations have gradually restricted the production and use of PFOA, trace residues may still be present in some commercially available products. Furthermore, during product use, these residues are continuously released into the environment and food through wear and aging. The International Agency for Research on Cancer (IARC) has now classified PFOA as a Group 1 carcinogen, and the cumulative health risks associated with long-term, low-dose exposure have been confirmed by the scientific community. Therefore, while regulatory oversight must be continuously strengthened, we must move beyond the static regulatory approach focused solely on initial residue levels in finished products and establish new standards that place greater emphasis on human health.

Furthermore, in response to the recent incident of alleged excessive PFAS levels in products from an international apparel brand, we performed relevant verification using the sensing device developed in this work. We selected commercially available outdoor jackets with waterproof coatings from 12 well-known sports and outdoor brands, as well as waterproof series products and popular yoga leggings from the aforementioned international brand, as experimental samples for testing. The leachate of cut fabric pieces with a total area of 1 cm^2 (5 mm $\times$ 5 mm fragments from multiple sites of each garment) was used as the final analytical object for the experiments (Fig. 6(h)). The results showed that no PFOA was detected in the two samples explicitly labeled with fluorine-free waterproof coatings, which was consistent with the product claims. However, PFOA levels exceeding the regulatory limit (1 $\mu\text{g/m}^2$) were detected in as many as six samples only labeled with waterproof function without specifying the waterproof technology, which met the criterion for non-compliant intentional addition, including high-priced products at the thousand-yuan level (Fig. 6(i) and Figs. S16(a)–S16(l) in the ESM). It is worth noting that no PFOA was detected in the waterproof series products of the aforementioned widely concerned international brand, as well as in the crotch and leg parts of its yoga leggings (Fig. 6(j), and Figs. S16(m)–S16(o) and Table S6 in the ESM). Therefore, for functional textile consumer products that are in frequent daily contact with the public, it is necessary to require relevant manufacturers to regularly provide compliant product test reports. In addition, for consumers,

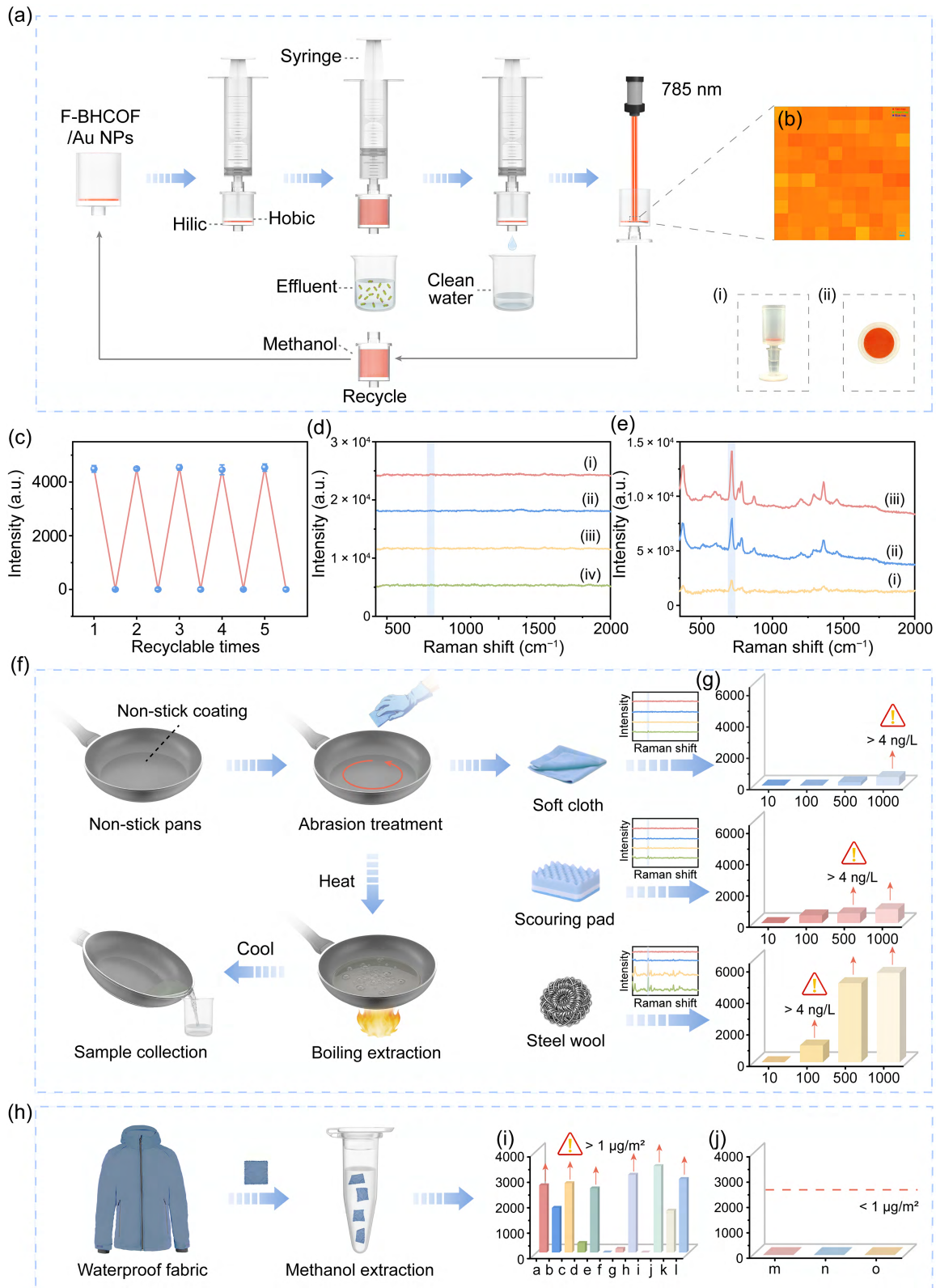


Figure 6 (a) Schematic showing the assembly, adsorption and detection, and reuse of device. (b) Mapping images of PFOA on the detection substrate of F-BHCOF/Au NPs. (c) The corresponding SERS intensities of 719 cm^{-1} peak when the CCGA aerogel was recycled 5 times for the detection PFOA. (d) SERS spectra of (i) commercial drinking water, (ii) water, (iii) soil, and (iv) algae from Lake LiHu. (e) SERS spectra in common water samples with different live of PFOA: (i) 10, (ii) 100, and (iii) 1000 ng/L. (f) Schematic of sample processing for non-stick pan abrasion test. (g) SERS spectra and bar charts of the leachates obtained after scrubbing non-stick pans with a soft cloth, scouring pad, and steel wool for 10, 100, 500, and 1000 cycles. (h) Schematic of sample processing for waterproof fabric test. (i) Bar charts of leachates obtained from commercially available waterproof coated outdoor jackets of 12 domestic brands a-l. (j) Bar charts of leachates obtained from the waterproof series products (m), crotch (n), and leg (o) parts of yoga leggings of the targeted international brand.

it is recommended to prioritize products explicitly labeled with fluorine-free waterproof coatings, or request sellers to provide recent and valid test reports at the time of purchase to avoid potential exposure risks.

4 Conclusion

In summary, based on the regulation at the molecular, surface/interface, and electronic structure levels, this study designed and synthesized F-BHCOF/AuNPs via the “amorphous-to-crystalline induced transformation” method and an *in-situ* reduction strategy, successfully constructing an eddy-assisted SERS platform enhanced by bowl-shaped confinement and polarization induction that integrates efficient PFOA adsorption and highly sensitive SERS detection. This material exhibits outstanding adsorption performance toward PFOA, demonstrating rapid adsorption kinetics and near-complete removal efficiency even at environmentally relevant concentrations (1 µg/L). Detailed investigations elucidated the fundamental contribution of the hydrophobic interface and F-F interactions after fluorine functionalization at the molecular level, as well as the “eddy effect” at the surface/interface level that enhances mass transfer and enrichment at low concentrations. For SERS detection, theoretical calculations and simulations were employed to analyze the dual “confinement effects” inside and outside the bowl-shaped structure at the surface/interface level, which synergistically enhance the electromagnetic field to improve detection sensitivity, as well as the “polarization induction” mechanism at the electronic structure level that mediates photoinduced charge transfer to achieve specific detection. Ultimately, the SERS limit of detection reached as low as 1.6 ng/L, which is superior to the latest standard issued by the U.S. EPA. This system effectively addresses the critical unmet needs of achieving nearly thorough adsorption and accurate SERS detection of PFOA, which are caused by the inherent molecular characteristics of PFOA, namely weak binding affinity to substrates, low intrinsic Raman activity, and high structural similarity among its homologs. Benefiting from these superior performances, this platform can be directly applied to the rapid screening and risk assessment of human exposure sources in environmental and daily consumer scenarios, and can be further extended to advance the development and improvement of analytical systems for routine *in-situ* monitoring and migration pathway elucidation of other hard-to-adsorb pollutants with low Raman response in water.

Electronic Supplementary Material: Supplementary material (experimental sections; temperature-dependent SEM images and NLDFT pore size distribution for understanding the formation of F-SSCOF, F-SHCOF, F-BHCOF; temperature-dependent SEM, TEM images for understanding the formation, PXRD patterns, FT-IR spectra and XPS curves of SSCO, SHCOF, BHCOF; adsorption kinetics pseudo-second-order fitting to high and low concentrations of PFOA by F-SHCOF and F-BHCOF; adsorption isotherm data fitted to the Freundlich model for F-SHCOF and F-BHCOF; COMSOL multiphysics modeling of PFOA adsorption into F-SSCOF and F-SHCOF; FT-IR spectra and XPS curves of F-BHCOF/AuNPs; NLDFT pore size distribution of F-BHCOF/AuNPs; TEM images, PXRD patterns, FT-IR spectra and XPS curves of F-SHCOF/AuNPs; the loadings plot of PC1 and PC2; SERS spectrum of the mixed interfering solution; refractive index and extinction coefficient spectra of F-BHCOF; UV-Vis

diffuses reflection spectra of F-BHCOF and UPS spectra of F-BHCOF at 0 V bias; photograph of the portable integrated adsorption-SERS detection device for PFOA; SERS spectra of leachates obtained from waterproof fabric; kinetic fitting results of high and low concentrations of PFOA on F-SHCOF and F-BHCOF; adsorbent, adsorption rate constant and PFOA kinetics concentration in this study and other reports in the literature; thermodynamic fitting results of PFOA on F-SHCOF and F-BHCOF; comparison of PFOA-sensor materials reported in recent literatures; detection of PFOA in sample using the SERS sensors; basic characteristics of tested textile samples and their PFOA detection results; calculation of work function, valence band and conduction band energy levels) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908994>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declarations of competing interest

All the contributing authors report no conflict of interests in this work.

Author contributions statement

F. L. L.: Conceptualization, investigation, visualization, writing – original draft. Y. J.: Software, resources, methodology, investigation. H. H. B.: Resources, supervision. Y. F. K.: Conceptualization, investigation. H. S. W.: Resources, supervision. X. D.: Validation, data curation. J. C.: Resources, supervision. H. M. Z.: Investigation, formal analysis, data curation. W. J.: Supervision, data curation. T. C. Z.: Writing – review & editing, supervision, resources, conceptualization. Y. F. X.: Supervision, funding acquisition, project administration.

Use of AI statement

None.

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