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Natural Deposition Strategy for Interfacial, Self-Assembled, Large-Scale, Densely Packed, Monolayer Film with Ligand-Exchanged Gold Nanorods for In Situ Surface-Enhanced Raman Scattering Drug Detection

Mei Mao,[a, b] Binbin Zhou,[a, b] Xianghu Tang,[a] Cheng Chen,[a] Meihong Ge,[a, b] Pan Li,[a] Xingjiu Huang,[a] Liangbao Yang,[a] and Jinhuai Liu[a]

Abstract: Liquid interfacial self-assembly of metal nanoparticles holds great promise for its various applications, such as in tunable optical devices, plasmonics, sensors, and catalysis. However, the construction of large-area, ordered, anisotropic, nanoparticle monolayers and the acquisition of self-assembled interface films are still significant challenges. Herein, a rapid, validated method to fabricate large-scale, close-packed nanomaterials at the cyclohexane/water interface, in which hydrophilic cetyltrimethylammonium bromide coated nanoparticles and gold nanorods (AuNRs) self-assemble into densely packed 2D arrays by regulating the surface ligand and suitable inducer, is reported. Decorating AuNRs with polyvinylpyrrolidone not only extensively decreases the charge of AuNRs, but also diminishes repulsive forces. More importantly, a general, facile, novel technique to transfer an interfacial monolayer through a designed in situ reaction cell linked to a microfluidic chip is revealed. The self-assembled nanofilm can then automatically settle on the substrate and be directly detected in the reaction cell in situ by means of a portable Raman spectrometer. Moreover, a close-packed monolayer of self-assembled AuNRs provides massive, efficient hotspots to create great surface-enhanced Raman scattering (SERS) enhancement, which provides high sensitivity and reproducibility as the SERS-active substrate. Furthermore, this strategy was exploited to detect drug molecules in human urine for cyclohexane-extracted targets acting as the oil phase to form an oil/water interface. A portable Raman spectrometer was employed to detect methamphetamine down to 100 ppb levels in human urine, exhibiting excellent practicability. As a universal platform, handy tool, and fast pretreatment method with a good capability for drug detection in biological systems, this technique shows great promise for rapid, credible, and on-spot drug detection.

Introduction

Self-assembly of nanoparticles (NPs) into densely arranged 2D nanoarrays has attracted much attention owing to distinctive chemical and physical properties that have led to a wide range of potential applications in optoelectronic devices,[1] chemical sensors,[2] catalysis,[3] and enhanced spectroscopy.[4] Due to the widespread application of densely packed nanofilms, an efficient and universal technique for the fabrication of large-scale, high-quality nanostructures is urgently required. At present, various approaches are feasible to prepare self-assembled NPs, including the use of a Langmuir–Blodgett (LB) trough,[5] lithographic patterning,[6] bottom-up assembly,[7,8] template-mediated assembly,[9] and evaporation-induced methods.[10] However, these methods suffer from high cost, low throughput, and rely strongly on sophisticated devices. Consequently, self-assembly at the liquid/liquid interface is among the most convenient, fast, and cost-effective techniques to construct uniform nanomaterials. The spontaneous assembly of NPs at liquid/liquid interfaces is due to the minimization of interfacial energy.[11] The liquid/liquid interface is prominent because it arises spontaneously without engineering, and the functional liquid nanofilm is usually uniform, self-healing, and defect-free.[12]

In recent decades, reports on the interfacial 2D self-assembly of spherical gold nanoparticles (AuNPs) occupied most of the market. Gold nanorods (AuNRs), as typical anisotropic particles, possess unique optical and electronic properties,[13] and are suitable self-assembled structures because their collective plasmonic properties depend on local density and orientation.[14] Assembled AuNRs displayed extremely high electromagnetic fields to yield enhanced optical signals.[15] Hydrophilic cetyltrimethylammonium bromide (CTAB) usually acts as a surfactant...
Moreover, CTAB is an amphipathic molecule, capable of interacting with both aqueous and organic phases, and thus, AuNRs barely achieve self-assembly at the liquid interface. AuNRs would undergo irreversible aggregation after CTAB removal from the surface of particles without further surface modification. Therefore, an adjusted surfactant that stabilizes AuNRs and can be used for interface assembly is essential. Zhou et al. showed that extremely stable, polyvinylpyrrolidone (PVP)-stabilized AuNPs successfully assembled at the interface. Exploiting PVP as a substitute for CTAB not only retained the morphology of AuNRs, but decreased the potential of the sol to promote AuNR assembly at the interface. In addition, PVP-stabilized Au NRs can be dispersed in ethanol. Ethanol plays two roles: one as a dispersant, and the other as an inducer to boost the formation of an interfacial film of AuNRs.

A tremendous challenge in the exploitation of self-assembled nanofilms at interfaces, compared with solid interfaces, is that they cannot be employed directly in various instances. Currently, typical methods of transferring interfacial films to substrates are horizontal and vertical lift-off, in which the substrate is immersed into the solution at a suitable angle. Sun et al. indicated that a smaller angle was more favorable for film transfer. The Langmuir method is a common means to obtain films. However, the interface film is always damaged to some degree and goes against the principle of obtaining large-scale densely packed NPs. What we cannot ignore is that targets can be detected directly at the interface without the transfer of the interfacial film. Ma et al. presented a liquid interfacial surface-enhanced Raman scattering (SERS) platform utilizing self-assembled NPs at cyclohexane/water interface for detecting trace drugs in human urine. Notably, it is difficult to find molecules that satisfy the requirements for directly participating in the process of assembled film and then located at the plasmonic hotspots. Therefore, it is essential to develop a feasible method to transfer or exploit the interfacial film.

Herein, we propose a novel strategy to fabricate self-assembled, large-scale, densely packed AuNR monolayers at the cyclohexane/water interface, and transfer the interfacial film with a skilled technique. A pivotal step of the surface exchange of AuNRs with PVP was introduced to eliminate the disadvantages of assembling CTAB-stabilized AuNRs. The technique is also applicable to different morphologies of NPs with CTAB as the surfactant. The self-assembly of CTAB-stabilized AuNPs at an interface was also demonstrated. Furthermore, by adopting a specially designed in situ reaction cell linked to a microfluidic chip, the self-assembled nanofilm could automatically settle on the substrate and be directly detected by means of a portable Raman spectrometer. The close-packed monolayer of self-assembled AuNRs provided massive, efficient hotspots to create a significant SERS effect to ensure sensitivity and reproducibility as a SERS-active substrate. In addition, the in situ reaction cell is also regarded as a reactor. If the target molecules are dissolved in aqueous or oil phases that form an interface, the molecules will migrate to the interface and adsorb spontaneously on the surface of the NPs during the assembly process due to Brownian motion and thermal disturbance. As a result, a 2D SERS platform of an assembled AuNR nanofilm deposited in the reaction cell in situ can be used directly for analyte detection. Based on our previous work for a 3 min pretreatment of urine samples from drug addicts we achieved a rapid, sensitive, and highly repeatable approach to detect drugs, even dual-phase and analyte detection. As a universal platform, handy tool, and fast pretreatment method with a good capability for drug detection in biological systems, this technique shows great promise.

Results and Discussion

Principle of AuNR self-assembly at the liquid interface

A crucial procedure for self-assembly at an interface is emulsification, in which water and oil are mixed in the presence of an inducer. CTAB is an ionic and amphipathic molecule, which usually acts as a surfactant in the synthesis of AuNRs, and is capable of interacting with both aqueous and organic phases. The self-assembly of NPs at the liquid/liquid interface depends on a number of factors, such as 1) the characteristics of the NPs, including size, charge, and surface ligand; 2) selection of an oil phase; 3) effect of the inducer; and 4) electrolyte concentration and pH. Thus, AuNRs rarely achieve self-assembly at the liquid interface, so it is imperative to supersede the surface-active agent. Additionally, an appropriate final concentration of CTAB after centrifugation is extremely important for successful substitution because a high concentration reduces the efficiency of ligand exchange and a low concentration is incapable of stabilizing the AuNRs, and even results in rapid accumulation. Herein, we employed AuNRs capped with PVP ligands, instead of CTAB, as shown in Figure 1A. PVP is a stable nonionic polymer that can be used in polar organic solvents and is easily soluble in water. Furthermore, the oxygen atom in the pyrrolidone is partially negatively charged, and thus, inclined to interact with cationic surfactants and the aqueous AuNRs–CTAB colloids, which display a positive charge. Thus, AuNRs–PVP is more favorably self-assembled at the interface because PVP modification reduces the charge on the surface of the NPs.

After ligand exchange between CTAB and PVP, the properties of the AuNRs are analyzed by UV/Vis absorption spectra. Figure 1B shows the absorption spectra of AuNRS–CTAB in water and AuNRs–PVP in ethanol; the extinction maximum does not shift, but the potential changes greatly. PVP-stabilized AuNRs displayed a negative potential and the zeta potential of the AuNRs decreased from +44.1 to −30.3 mV after the surfactant was replaced (Figure 1C). In general, the colloid can maintain stability if the zeta potential is between ±30 and ±60 mV. This evidence clearly demonstrates the successful substitution of CTAB and PVP on the AuNRs. Furthermore, the surface chemical elements of AuNRs were investigated by XPS. As shown by the high-resolution N 1s XPS spectra (Figure 1D), the peaks at 402.23 and 399.66 eV, which are assigned to CTAB and PVP, respectively. Figure 1E shows the high-resolution XPS spectra of CTAB and PVP on the AuNRs.
tion O 1 s XPS spectra; there is only a single peak at a binding energy of 531.22 eV, which is attributed to PVP, because CTAB does not contain oxygen. The XPS spectra suggested that CTAB was exchanged with PVP, and the PVP molecules were strongly adsorbed on the AuNR surface. After ligand exchange, there is a significant difference in the resonances of the background signals of SERS substrates: for AuNRs–CTAB in a dry membrane, two main signals appear at 780 and 1440 cm$^{-1}$, by contrast, in our system, dry AuNRs–PVP has only one characteristic signal and a smoother baseline, which may, to some extent, be good for detection (Figure 1 F and G).

The driving force for the bulk NPs attaching to the oil/water interface is the minimization of the Helmholtz free energy, as shown in Scheme 1. As anisotropic AuNRs, the geometric configurations at the interface are varied. The two most typical arrangements are parallel and perpendicular to the interface and the change in the interfacial energy is given by Equations (1)–(3):

$$\Delta E_{\text{int}} = 2RL[(\pi - \theta)(\gamma_{\text{AuNR}/o} - \gamma_{\text{AuNR}/w}) + \gamma_{\text{o/w}} \sin \theta]$$

$$\cos \theta = \frac{\gamma_{\text{AuNR}/w} - \gamma_{\text{o/w}}}{\gamma_{\text{o/w}}}[H \gg R]$$

$$\Delta E_{\text{L}} = (\gamma_{\text{AuNR}/w} - \gamma_{\text{o/w}} - \gamma_{\text{AuNR}/o})2\pi R^2 + (\gamma_{\text{AuNR}/w} - \gamma_{\text{o/w}})2\pi Rh$$

in which $R$ is the radius of the AuNRs; $H$ is the length of the AuNRs; $\gamma$ is the interfacial energy; $\theta$ is the contact angle of the AuNRs at the interface; $h$ is the depth of AuNRs in the water phase, if placed vertical to the interface; and $o$ and $w$ indicate oil and water, respectively.

Based on previously estimated values, for AuNRs oriented parallel to the interface, the contact angle is over 3.4 times greater and the interfacial energy is 40 times lower than that of AuNRs perpendicular to the interface. Therefore, the geometric configuration of AuNRs at the interface is parallel to the interface, with a tendency to assemble side-by-side, so that as many NRs surround Au as possible.

Significance of self-assembled monolayers at the interface and practicability of the “natural deposition” transfer technique

A compact, monolayered, 2D AuNR film self-assembled at the cyclohexane/water interface was successfully fabricated. For a long time, the challenge was how to transfer the interfacial film. Normally, electrostatic attractions allow tweezers to adhere to the film, but this causes mechanical disturbance at the interface (Scheme 2B). The slow downward movement of the interface onto a fixed substrate weakens the mechanical disturbance; thus maintaining the integrity of the film. To preserve the large-scale order of the interfacial films, we propose a novel deposition method, natural deposition, as presented in Scheme 2C. By employing this strategy, large-scale monolayer AuNR films have been attained. As shown in Figure 2, the film deposited on silicon wafer was treated by two different methods. Large areas of cracks emerged on the AuNR film upon
using traditional tweezers, whereas, in contrast, no visible voids were observed over the whole film through natural deposition. This result revealed the capacity of the natural deposition technique to fabricate large-scale, monolayered AuNRs films. The morphology and structure of the AuNRs were characterized by SEM. The SEM images in Figure 2B clearly show a large area and well-ordered, close-packed, monolayered AuNR film. The AuNRs mostly assemble side-by-side in the SEM images. The monolayered close-packed film confirmed the interparticle distances of adjacent AuNRs that provided massive hotspots; thus the structure of the self-assembly produced uniform SERS enhancement. However, compared with AuNP films fabricated by means of the traditional method, the distribution of the AuNRs is far from homogeneous and the number of void areas is significantly increased (Figure 2D). Moreover, different concentrations of AuNRs were explored to observe the area of nanofilm. If the ligand was not substituted, small regions generated film at the interface (Figure S2 in the Supporting Information). By contrast, AuNRs–PVP at a concentration from 0.1 to 1.0 μM successfully realized an expansive metallic interfacial film. Hexane was also an ideal oil phase to achieve self-assembly of AuNRs (Figure S3 in the Supporting Information). In addition, AuNPs–CTAB could also self-assemble at the cyclohexane/water interface by utilizing ligand exchange from CTAB to PVP, with which a large-area monolayer emerged from the interface. Additionally, traditional methods and natural deposition were used to gather the NPs, but the results were very different (Figure S4 in the Supporting Information). SEM images and distance–distribution histograms of the interparticle gap further confirmed the homogeneity and compactness.

A Raman spectrometer was also used to reveal the uniformity and integrity of two patterns of AuNRs (Figure 3A, C). As observed, a homogeneous macroscopic structure is obtained with the natural deposition strategy (Figure 3A), but several fissures appear with the traditional method (Figure 3C). To further assess the reproducibility of the 2D self-assembled film as SERS substrates, a 20 μm × 20 μm area obtained by means of the two methods are then mapped by point-by-point scanning with a step size of 1 μm (20 × 20 spots each) during laser excitation. The average signal intensity (I_{ave}) at 913 cm⁻¹ from the 400 spots was measured and the relative standard deviation (RSD) of these SERS intensities was also calculated (Figure 3B, D). The average signal intensity of the test area of the 3D superlattice array is about 2650.4 counts with an RSD of only...
7.8%, whereas the film transferred with tweezers has an average signal intensity of only 1379.6 counts with an RSD as large as 86.3%. These results demonstrate the feasibility of the automatic self-assembly deposition method, with good reliability and reproducibility. To compare the performance of the substrate, untreated Au NRs obtained by centrifugation and drying were also measured to obtain the reference information. The signals of SERS spectra for different concentrations of CV from $10^{-1}$ to $10^{-8}$ M with the self-assembled 2D array and dry AuNRs were recorded (Figure S5 in the Supporting Information). The SERS intensity of CV was still distinctly identified at $10^{-5}$ M, whereas faint signals of $5 \times 10^{-9}$ M CV appeared for the dry AuNRs; this indicates that the 2D interfacial SERS platform acquired by natural deposition exhibits good SERS activity and sensitivity as a SERS substrate.

**Sensitivity and reproducibility of the self-assembled monolayer for in situ drug detection**

Currently, the rapid identification and detection of drugs for public security enforcement have great significance. SERS as a reliable molecular vibrational detection method holds great promise for use on complex biological systems due to high sensitivity and selectivity. Owing to miniaturization, portability, and large spot area, a portable Raman spectrometer has been widely applied to drug abuse,[24] pollutants,[25] explosives,[26] and food safety.[27] Herein, a portable Raman spectrometer was used to verify the practicality of the 2D self-assembled interfacial SERS platform. To examine the reliability and sensitivity of the SERS platform, characteristic SERS spectra of methamphetamine (MA) extracted from human urine at different concentrations from 100 ppb to 100 ppm were recorded (Figure 4A). The intensities of the SERS spectra progressively increase in accordance with increasing concentration of MA. Remarkably, the portable Raman spectrometer has more advantages for detecting MA with the 2D self-assembled interfacial SERS platform, compared with a Lab-RAM HR800 spectrometer. Two main factors may contribute to this result: one is the larger spot area being irradiated on the SERS-active substrate and target molecules. The area of the laser spot of the portable Raman spectrometer is approximately 100 $\mu$m$^2$, which is broader than that...
in laser confocal Raman spectroscopy (laser spot of about 1 μm²), and receives more signal from MA per time unit. The other factor is the massive number of SERS hotspots. The 2D self-assembled interfacial film is monolayered and compact, which enables more target molecules to be located in the regions of the hotspots; in particular, anisotropic AuNRs create more hotspots in our SERS platform and produce greater electromagnetic enhancement. In addition, the designed cell achieved in situ detection due to self-assembled AuNRs being deposited at the bottom of the cell and the drug molecules participating in the assembly process being located at the hot spots. The characteristic bands of MA are clearly distinguished (620, 750, 834, 1003, and 1206 cm⁻¹).[28] The SERS bands at 620 and 1003 cm⁻¹ are attributed to the phenyl ring breathing mode; that at 834 cm⁻¹ is assigned to the C–C stretch of the isopropyl group; and those at 1206 and 1030 cm⁻¹ are due to phenyl–C stretching and C–H deformation of the phenyl ring, respectively. Our 2D SERS platform is able to detect MA at a concentration down to 100 ppb, which indicates good sensitivity by the portable Raman spectrometer.

To evaluate the practicality of the fabricated SERS substrates, we analyzed the repeatability and uniformity to determine suitable sensitivity. Hence, the SERS spectra of 100 ppm MA in human urine were collected from 30 random laser spots on the 2D SERS platform (Figure 4B). All of the spectra produced the characteristic fingerprint bands of MA molecules. The fluctuation of main characteristic band intensities of the MA molecule was statistically analyzed by wave patterns (Figure 4C, D), and the RSD of those intensities in each spectrum set was calculated as an indicator of signal reproducibility. The band at 1003 cm⁻¹ for 100 ppm MA produced an RSD value of 4.76%; and that for the band at 1206 cm⁻¹ was 8.35%; this revealed high repeatability of the 2D SERS platform. The 2D self-assembled interfacial SERS platform is reasonably believed to open up a new strategy of on-spot detection of MA, by combining the oversimplified, rapid, and reliable pretreatment of human urine with a portable Raman spectrometer detection system.

Applications of the 2D SERS platform to detect solo and dual analytes

To examine the versatility and sensitivity of the 2D SERS platform, different drugs dissolved in different solvent phase were detected that aqueous phase or oil phase to apply to assembly. Ketamine, commonly known as K, was increasing addicted by adolescent, therefore it is critical to rapid and accurate detection of ketamine. Hence, the concentration of 1 ppm to 10 ppm ketamine solution as water phase constructed the interfacial AuNRs arrays. Figure 5A shows the SERS bands at 458, 654, 1023, 1048, and 1593 cm⁻¹, which are attributed the vibrations of bonds of ketamine;[29] details are given in Table S1 in the Supporting Information. We also investigated oil-soluble MDMA extracted from human urine at concentrations of 1 and 10 ppm. Figure 5B shows the SERS spectra of MDMA, with characteristic bands at 716, 812, 1248, 1360, 1496, and 1628 cm⁻¹,[30] for which the bands are clearly observed at concentrations as low was 1 ppm. Several analytes at different concentrations were successfully detected; this further highlights the versatility of the 2D SERS platform.

The above work revealed that individual analytes dissolved in either the aqueous or organic phases were successfully detected by the 2D self-assembled SERS platform. Furthermore, we examined the capability of 2D AuNRs arrays for dual-phase and dual-analyte detection, which implied that both aqueous- and organic-phase-soluble analytes were detected simultaneously. In detail, water-soluble CV and MDMA were chosen for aqueous-phase detection, and MA, which was extracted from human urine and dissolved in cyclohexane, was also located the same system. A solution containing CV (1 mL, 5 ppb) and MA (1 mL, 10 ppm) extracted from human urine formed an water/oil interface, and then a solution (1 mL of AuNRs–PVP in ethanol was added to induce interfacial self-assembly of the 2D SERS platform for subsequent identification and detection. As shown in Figure 6A, dual-phase and -analyte detection of CV in water and MA in cyclohexane is possible by distinguishing each signal compared with that of solo analyte detection. Then MA and MDMA, which are two commonly used amphetamine derivatives, were dissolved in oil and aqueous phases separately for detection by the 2D self-assembled SERS platform. Solutions of MDMA (1 mL, 20 ppm) and MA (1 mL, 10 ppm) were mixed to obtain aqueous and oil layers. The SERS spectra revealed the characteristic Raman bands of both MA and MDMA in single- and dual-analyte detection (blue line in Figure 6B). The bands at 716, 812, 1248, 1360, 1496, and 1628 cm⁻¹ can be explicitly assigned to MDMA, whereas those at 620, 1001, 1030, and 1208 cm⁻¹ are attributed to MA. The results indicated the excellent capability of dual-phase and -analyte detection by using this 2D self-assembled SERS platform.
Experimental Section

Synthesis of AuNRs–CTAB in water

AuNRs were synthesized through improving upon typical seed-growth methods, including procedures for the preparation of seed and growth solutions. First, to prepare the seed solution, a 0.1 M solution of CTAB (10 mL) was added to a 25 mL round-bottomed flask in a constant-temperature water bath at 28 °C. Then, a 25 mM solution of HAuCl₄ (0.1 mL) was slowly added to the mixture under stirring, and a freshly prepared 0.01 M solution of NaBH₄ (0.12 mL) was added and the color of the solution turned to pale yellow. The color of the mixture changed from yellow to brown after vigorously stirring for 1 min, and the seed solution was allowed to stand in the water bath. Next, to complete the preparation of the growth solution, a 0.2 M solution of CTAB (10 mL) was prepared in a 25 mL conical flask, and then a 0.01 M solution of AgNO₃ (0.12 mL) was added under gentle stirring. Subsequently, solutions of HAuCl₄ (0.2 mL, 25 mM) and HNO₃ (0.1 mL, 2.0 M) were added to the reaction solution. Following the addition of AA (0.06 mL, 0.1 M), the solution changed from yellow to colorless, which indicated that Au³⁺ was reduced to Au⁰. Finally, the abovementioned seed solution (12 µL) was added under gentle mixing for 0.5 min. The AuNRs were obtained after heating for 24 h at a constant temperature of 30 °C.

Surface ligand exchange of AuNRs–CTAB with PVP

The freshly prepared solution of AuNRs–CTAB (12 mL) was centrifuged at 8000 rpm for 10 min and washed twice with ultrapure water to remove excess CTAB. Then, a solution of the protective agent in organic phase was prepared by dissolving PVP (6 mg) in ethanol (12 mL). The centrifuged AuNR products were dispersed in the solution of PVP in ethanol and stirred for 12 h at 600 rpm for the purpose of exchanging the surface ligand entirely. The final solution of AuNRs–PVP was concentrated in ethanol (6 mL) and used for the self-assembly experiments.

MA extraction from human urine

The experimental human urine came from the CAS Hefei Cancer Hospital, and was purified according to previous work. Briefly, urine (1.0 mL) was mixed with drug (1.0 mL) of different concentrations in a 4.0 mL Eppendorf tube (see Figure S1 in the Supporting Information). In general, the drug molecules in the aqueous solution were in the form of hydrochlorates, and therefore, a 5% solution of NaOH (200 µL) was added to neutralize the acid. One of obstacles that affected drug purification from urine was urea, so the addition of NaCl (0.68 g) precipitate the protein. Herein, the salt also played two other roles: one was to greatly increase the drug concentration. Owing to the addition of NaCl, the solution was saturated, so the moisture content decreased. The other role of salt was that NaCl acted as a demulsifier. Cyclohexane (200 µL) as the extraction solvent was added to extract drug molecules from the human urine. Finally, the Eppendorf tube has been vigorously shaken, allowing the organic layer to separate spontaneously. The organic layer (100 µL) containing drugs was ultimately removed from the tube by pipette and the whole purification process was achieved in 3 min.

Self-assembly of AuNRs at the liquid/liquid interface and in situ acquisition through the natural deposition strategy

The SERS platform of the liquid/liquid interfacial self-assembly of AuNRs in cyclohexane/water was inspired by a report in the litera-
First, the ligand on the AuNRs was replaced with PVP to not only extensively decrease the charge of the AuNRs, but also diminish repulsive forces (Scheme 2A). Specifically, an appropriate volume of H2O was added to the designed in situ reaction cell until the bottom of the vessel was filled. The bottom of the reaction cell was fitted to the microfluidic device with a circulation pump. The substrate, such as silicon wafer or glass, was embedded in the reaction cell. The sealed environment around the wafer guaranteed that we could regard it as an assembly container. Then, cyclohexane was dropped over the layer of water and an incompatible cyclohexane–water liquid interface appeared. Additionally, we used cyclohexane containing drugs extracted from human urine. Subsequently, AuNRs–PVP (12 mL) was centrifuged at 7500 rpm for 10 min to collect the precipitants and then diluted with ethanol (4 mL), which was added slowly to the interface. Ultimately, the AuNR-trapped drugs spontaneously self-assembled into a highly close-packed film over a large area at the cyclohexane/water liquid interface with the evaporation of cyclohexane. Remarkably, the self-assembled AuNR SERS platform embodying drugs was also suitable for detecting targets dissolved in aqueous solution. In our system, microfluidic access sucked out the lower aqueous phase after AuNRs assembled at the interface, accompanied by volatilization of the upper oil phase, so that the self-assembled nanofilm sank into the substrate. The interfacial self-assembled NPs were deposited completely on the silicon wafer placed on the bottom of the vessel, as illustrated in Scheme 2C. This technique ingeniously avoided the need for a suitable method to transfer the interfacial film.

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Conflict of interest

The authors declare no conflict of interest.

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References


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