

# Metal organic framework wrapped gold nanourchin assembled on filter membrane for fast and sensitive SERS analysis

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## ABSTRACT

Plasmonic particle-metal organic framework hybrid received considerable attention in SERS analysis. However, most detection procedure suffers from long immersion time, low enhancement, and random substrate aggregation. To improve detection efficiency, sensitivity and reproducibility, gold nanourchins wrapped with metal organic framework MIL-100(Cu) (GNU@MOF) were prepared and assembled onto a filter membrane to develop a filtration detection mode. The substrate-analyte interaction time reduces from 60 min in immersion mode (GNU@MOF-I) to 10 s in filtration mode (GNU@MOF-F). Interestingly, the SERS signal on GNU@MOF-F is comparable or 1-7 folds higher than that on GNU@MOF-I, depending on analyte concentration. Detection limit for toxic dye MG on GNU@MOF-F is 0.1 nM, which is 10- or 100-fold lower than that on GNU@MOF-I (60 min or 10 s). The signal reproducibility was also improved on GNU@MOF-F ( $RSD < 13\%$ ) compared with that on GNU@MOF-I ( $RSD > 30\%$ ). Comparison experiments reveal the improvement can be ascribed to the filtration induced enrichment of analyte together with even and dense assembly of GNU@MOF, which form more uniform and efficient hot spots. Similar results was found for practical detection of MB in lake water with good reusability. Such efficient SERS substrate with simple and fast operation holds great promise in chemical and environmental analysis.

## 1. Introduction

Surface enhanced Raman scattering (SERS) is a powerful analytic tool with promising application in various branches of analytical science [1,2]. An efficient substrate plays a dominated role in determining its sensing performance [3–6]. Recently, integrating Au or Ag nanostructures with other functional materials with magnetic, catalytic, porous, or flexible properties becomes a hot topic [7–13]. Specifically, hybrids of Au/Ag nanostructures with metal organic frameworks (MOFs) receive considerable attention [14–19]. The introduction of MOF not only improves sensitivity, but also endows the substrate with proper selectivity and makes it possible to detect analyte with low affinity to Au/Ag substrate owing to the tunable pore size, strong adsorption ability, and chemical enhancement effect of MOF [9]. Therefore, developing novel Au/Ag-MOF hybrid substrate is important and interesting for practical SERS analysis.

Despite the advantages of various hybrid substrate of Au/Ag-MOFs in SERS application, there is also many challenges and great space to be explored. (1) Most work use spherical particles to construct MOF-Au/Ag

hybrid [20,21], and few involves anisotropic particles, which may produce higher enhancement ability [22]; (2) to increase signal, Au/Ag particles are densely decorated onto MOF [21,23], which blocks the pores of MOF and brings uncontrolled aggregation; (3) longtime incubation from 30 min to 10 h is needed to improve SERS signal in typical immersion detection mode [21,24–26], which leads to low efficiency; (4) these MOF based substrates easily precipitate in solution or random aggregate on matrix (typically glass or silicon slide [20,21,25–27]), leading to poor signal reproducibility. On the other hand, filtration is a simple and effective way to separate or enrich molecules, and MOFs have intrinsic advantage for filtration, separation and enrichment [28]. However, the combination of MOF based hybrid substrate with filtration for SERS detection has not been reported.

In this study, gold nanourchins (GNUs) wrapped with metal organic framework (GNU@MOF) was prepared and assembled on filter membrane to achieve fast and sensitive SERS analysis. The combination of GNU and MOF (MIL-100(Cu)) provides higher enhancement than that of GNU or MOF in traditional immersion detection mode with detection time 60 min. To improve sensing efficiency, GNU@MOF was assembled

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on a filter membrane to develop a filtration type substrate GNU@MOF-F by simple filtration operation. For this substrate, the interaction time of substrate with analyte was greatly reduced from 60 min to less than 1 min (about 10 s). Interestingly, the SERS signal obtained on GNU@MOF-F is comparable or even stronger than those obtained on typical immersion mode substrate (GNU@MOF-I), and the signal reproducibility was also greatly improved. The GNU@MOF-F was used to detect toxic dye MG in standard solution and MB in lake water sample, which shows one or two orders of magnitude lower detection limit than that of GNU@MOF-I (60 min) or GNU@MOF-I (10 s). Moreover, the GNU@MOF-F can be reused at least 3 times without obvious signal attenuation.

## 2. Materials and methods

### 2.1. Reagents

Chloroauric acid ( $\text{HAuCl}_4$ ), trisodium citrate dihydrate ( $\text{Na}_3\text{Cit}$ ), silver nitrate ( $\text{AgNO}_3$ ), L-dopa, polyvinylpyrrolidone (PVP, K30), aluminum chloride hexahydrate ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ), copper(II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), nickel chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), methylene blue (MB), and malachite Green (MG) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were used as received without further processing. Deionized water ( $\rho \geq 18.2 \text{ M}\Omega \text{ cm}$ ) was produced by a Milli-Q equipment.

### 2.2. Instruments

Scanning electron microscopy (SEM) images were captured using an S-3400 SEM equipped with an energy-dispersive X-ray (EDX) analyzer (Hitachi, Japan). Transmission electron microscopy (TEM) images were obtained via a JEM-2100 F TEM (JEOL Ltd., Japan). Absorption spectra were measured using a U3900H UV-vis spectrophotometer (Hitachi, Japan). All Raman spectra measurements were performed on a LabRAM-HR Raman system (Horiba, Japan).

### 2.3. Materials preparation

#### 2.3.1. Synthesis of gold nanourchins (GNUs)

A facile silver nanoseed mediated approach was used to prepare gold nanourchins based on our previous method [29]. Details can be found in supporting information. The obtained GNUs were re-dispersed into 9 mL water.

#### 2.3.2. Preparation of GNU@MIL-100 (Cu)

GNU@MIL-100 (Cu) was prepared through a layer-by-layer growth method [30]. (1) 2 mg PVP dissolved in 0.2 mL water was mixed with 2 mL of GNU suspension and stirred for 4 h; the product was centrifuged, washed with DMF, and dispersed into 2 mL DMF to get the PVP modified GNUs. (2) 1 mL PVP modified GNU was added to 4 mL of 15 mM  $\text{CuCl}_2$  in DMF and sonicated for 10 min. The product was centrifuged and re-dispersed into 1 mL DMF. (3) 1 mL of the product of step (2) was mixed with 4 mL of DMF containing 15 mM BTC and reacted for 20 min. The product was centrifuged, washed twice with DMF and ethanol, dispersed into 1 mL of ethanol to obtain GNU@MIL-100(Cu) with one coating layer of MOF. Repeat the operation of step 2 and 3 to coat GNU with 2 or more layers of MOF shell.

#### 2.3.3. Preparation of filtration type substrate GNU@MOF-F

A simple filtration operation was used to assemble GNU@MOF onto filter membrane to form GNU@MOF-F. In brief, the nylon filter membrane (0.22  $\mu\text{m}$  pore size) was placed into a suitable syringe filter holder. Then, 10  $\mu\text{L}$  of GNU@MIL-100 (Cu) suspension was passed through the organic filter by a injector, leaving the GNU@MIL-100(Cu) on the filter surface. The prepared substrate was called GNU@MOF-F (F stands for filtration) for convenience in the following.

### 2.3.4. Procedure for SERS analysis

The original solution of analytes (MG, MB) ( $10^{-4} \text{ M}$ ) was prepared using ethanol as solvent and then diluted into different concentrations ( $10^{-5} \text{ M}$  to  $10^{-10} \text{ M}$ ) by water.

(1) In a typical immersion mode, 100  $\mu\text{L}$  of the substrate material (GNU or GNU@MOF) suspension was mixed with 400  $\mu\text{L}$  of the analyte solution and incubated for 60 min. Then the solid was separated by centrifugation, dropped onto a clean silicon wafer, and dried in air for Raman test. The substrate used in this mode was called GNU-I, GNU@MOF-I (I stands for immersion) for convenience in the following.

(2) In a filtration mode, 100  $\mu\text{L}$  substrate material suspension was first passed through the organic filter, leaving their assembly on the filter to form the substrate GNU-F or GNU@MOF-F. Then, 400  $\mu\text{L}$  of analyte solution was sequentially breathed into syringe and passed through the filter. The substrate with analyte was dried in air for SERS analysis.

For all Raman tests, a He-Ne laser with 633 nm wavelength and 1 mW power was used as the excitation source. The integration time was 5 s and an average of at least 5 measurements was presented for resulting Raman spectrum.

## 3. Results and discussion

### 3.1. Preparation and characterization of GNU@MOF

Branched gold or silver nanostructures often provide stronger SERS signal than their spherical counterpart. So, GNUs prepared by our previous Ag seed mediated method was used in this study. The GNU displays an urchin-like morphology (Fig. 1a) with many nano-thorns on its surface (Fig. 1b). The EDX result reveals the product is mainly composed of C, Au and a little Ag (Fig. 2a). Element C is from the reductant L-dopa as its oxidant product can adsorb onto GNU in a similar way to that of polydopamine's universal coating. Element Ag is from Ag seed, which is oxidized into  $\text{Ag}^+$  and reduced back to Ag by L-dopa to dope into the product (Fig. 2a) [31].

Coating MOF onto GNU was achieved through layer-by-layer assembly of metal ions ( $\text{Cu}^{2+}$ ) and BTC [30]. Fig. 1c shows the urchin-like morphology is retained after the MOF coating. Further amplified TME image indicates that a thin layer ( $12 \pm 5 \text{ nm}$ ) of light-colored matter was uniformly wrapped around the GNU (Fig. 1d). Corresponding XRD results reveal the GNU@MOF displays typical diffraction peaks for both Au and MIL-100(Cu) (Fig. S1). Element analysis shows the content of C increases and a new element Cu appears after coating MOF onto GNU (Fig. 2b). The absence of signal for Ag can be ascribed to its low content in the hybrid. Based on these results, it is believed that a core-shell type GNU@MIL-100(Cu) hybrid was successfully prepared.

The morphology and structure transformation were also reflected by UV absorption spectrum of different materials. As shown in Fig. S2, the absorption peak of Ag seeds locates at 418 nm, a typical surface plasmon resonance peak of spherical silver nanoparticles. After reaction with  $\text{HAuCl}_4$ , the absorption peak of AgNPs disappears, and a wide peak with maximum absorption out of the visible region appears. According to Halas [32], this broad absorption peak corresponds to a higher level of resonance absorption, indicating that product with non-spherical or non-smooth surface may be generated. The UV absorption spectrum of the GNU@MIL-100(Cu) likes that of GNU (Fig. S2), implying MOF coating does not obviously change its urchin-like structure.

### 3.2. SERS response in immersion mode

The Raman enhancement ability of materials in this work including AgNPs, GNU and GNU@MOF were investigated using malachite green (MG,  $10^{-5} \text{ M}$ ) as the probe molecule. These substrates are first tested in immersion detection mode as it is the most common procedure for SERS analysis by Au/Ag-MOF hybrid substrate in reference [20–27]. Fig. 3 shows all these materials can enhance the Raman scattering signal of MG

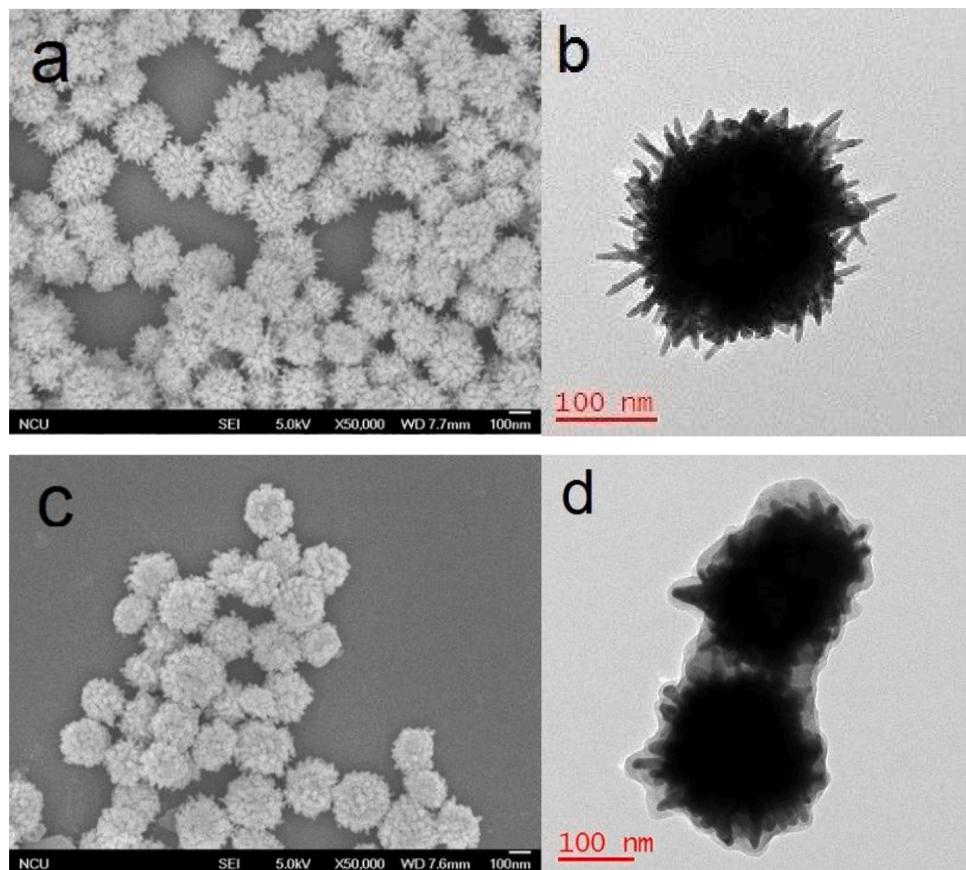


Fig. 1. SEM and TEM images of (a,b) GNU and (c,d) GNU@MIL-100 (Cu).

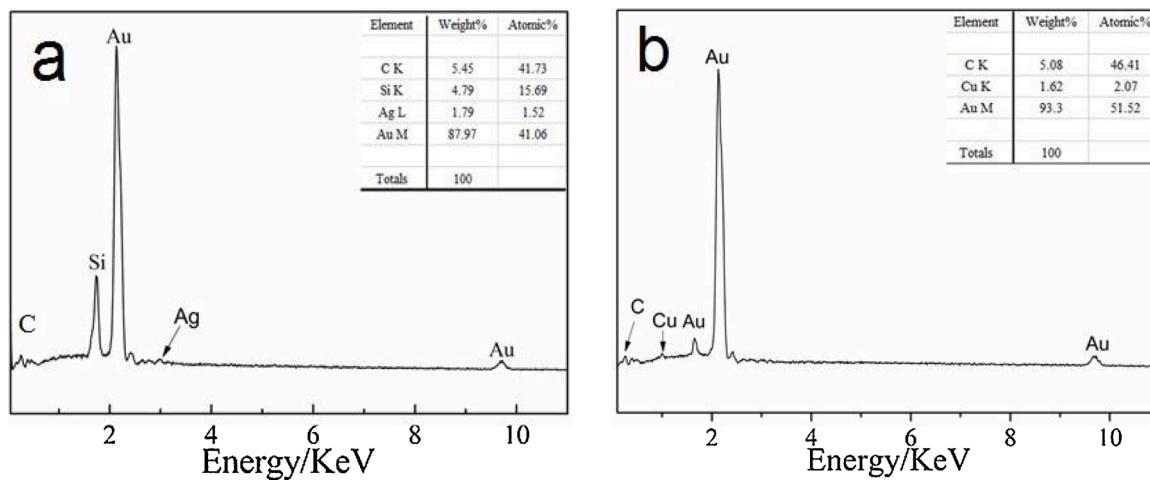
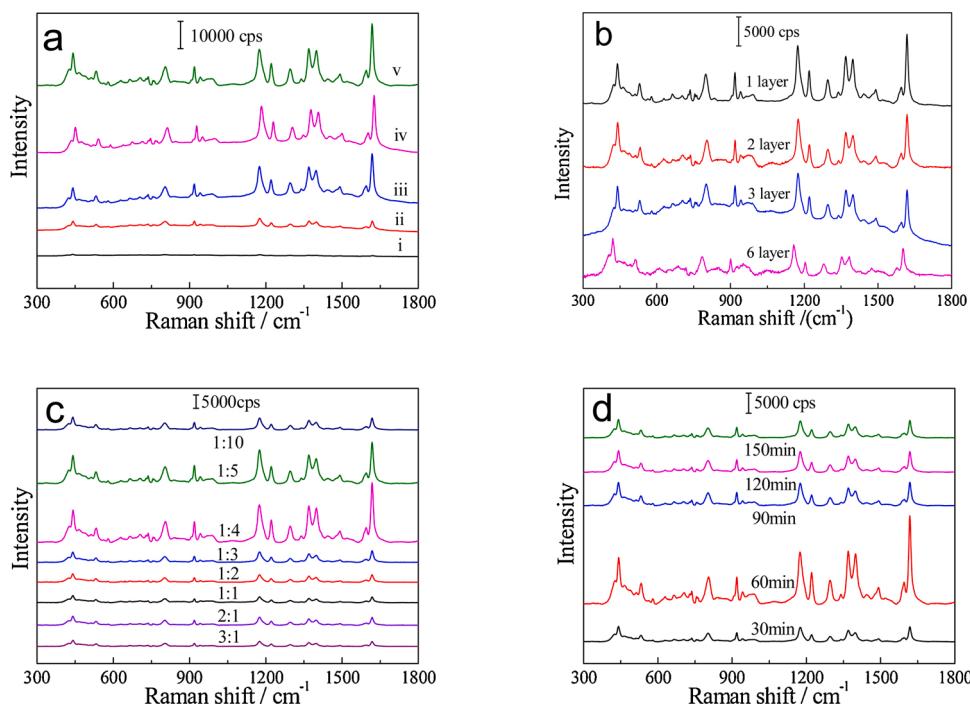


Fig. 2. EDS results for (a) GNU, and (b) GNU@MOF-MIL-100(Cu).

[33]. Detailed band assignment can be found in Table S1 in supporting information. For AgNPs as substrate (line i, Fig. 3a), the SERS signal is the weakest due to few hotspots formed by limited amount of AgNPs. The SERS signal is stronger on GNUs (line ii, Fig. 3a). The enhanced signal can be ascribed to increased hotspots formed by GNUs' plenty of nanothorns as reported before [31]. Interesting, the SERS signal further increases more than 5-fold after GNU is coated with a thin layer of MIL-100(M) (M = Al, Cu, Ni) (line iii-v, Fig. 3a). Among these GNU@MOFs, the GNU@MIL-100(Cu) presents the strongest signal (line v, Fig. 3a). Thus, in the following, GNU@MIL-100(Cu) was used for test.

The enhanced Raman signal of MG on GNU@MOF compared with

that on GNU can be ascribed to the chemical enhancement effect and enhanced adsorption of the MOF coating layer. UV-vis results indicate the absorption intensity of MG decreases after it was incubated with GNU-I or GNU@MOF-I (Fig. S3). The decreased amplitude on GNU@MOF-I is slightly higher (about 20%) than that on GNU-I. This result confirms MOF coating indeed increases the substrate's adsorption ability to analyte. But this effect's contribution to SERS signal is limited due to tiny thickness of MOF layer (Fig. 1d). Thus, it is believed the chemical enhancement from MOF shell plays a dominant role in enhancing the SERS signal compared with that of GNU [14]. In a word, the GNU@MOF displays the most efficient enhancement due to the



**Fig. 3.** SERS spectrum of MG obtained on (a) different substrates: (i) Ag seeds; (ii) GNU; (iii) GNU@MIL-100 (Al); (iv) GNU@MIL-100 (Ni) and (v) GNU@MIL-100 (Cu); (b) GNU@MIL-100 (Cu) coated with different cycles of MOF layer; (c) different volume ratio of GNU@MIL-100 (Cu) to MG; (d) GNU@MOF with different immersion time in MG aqueous solution.

combined effect of the GNUs core and the MOF shell.

### 3.3. Optimization of SERS analysis in immersion mode

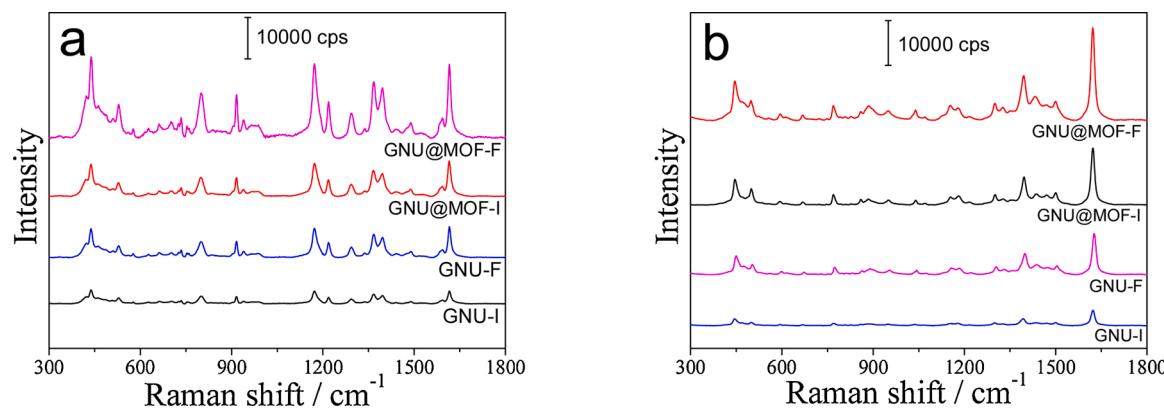
Previously, Au/Ag-MOF hybrid are often used in above mentioned “immersion mode” for SERS analysis. It is believed the introduction of MOF can capture or enrich analyte onto their surface and thus improve the signal intensity. Therefore, long time incubation is preferred or required to adsorb more analyte to obtain strong SERS signal. Here, several parameters including the immersion time of substrate in dye molecule solution, volume ratio of substrate suspension to analyte solution, and cycle number of MOF layer coating were investigated.

The effect of thickness of MOF shell on the SERS signal was first investigated. Fig. 3b shows the strongest SERS signal is obtained on GNU@MOF with only one coating circle (2 nm of MOF coating), and it gradually decreases as the coating circle increases. That means the thinner of the shell, the higher of the SERS signal. This is consistent to previous results for core-shell type Au/Ag-MOF hybrid [30,34], and further confirms the dominant role of electromagnetic enhancement (EM) effect of GNU in amplifying the SERS signal. Increasing coating circle of MOF generates thick MOF which results in two effects: increases the adsorption to analyte, but also increases the distance between the analyte and GNU. It seems that the two effects are balanced at the first three coating circles as the SERS signal does not show significant change for GNU@MOF with 1-3 coating layer. When it increases to six coating layers, the SERS signal decreases obviously, indicating the enhanced adsorption cannot compensate the attenuation of EM effect, leading to the decrease of SERS signal. Next, the volume ratio of substrate suspension to analyte solution was optimized. Fig. 3c shows the strongest SERS signal is obtained at 1:4. Further increasing the content of MG leads to decreased signal as less GNU@MOF and thus less hotspots are available for enhancement. Conversely, if the proportion of GNU@MOF increases, few MG molecules are available to generate SERS signal (Fig. 3c). Finally, the immersion time of GNU@MOF in analyte solution was optimized. Fig. 3d shows that the strongest SERS signal of MG is obtained at 60 min, a long incubation time. Similar longtime incubations

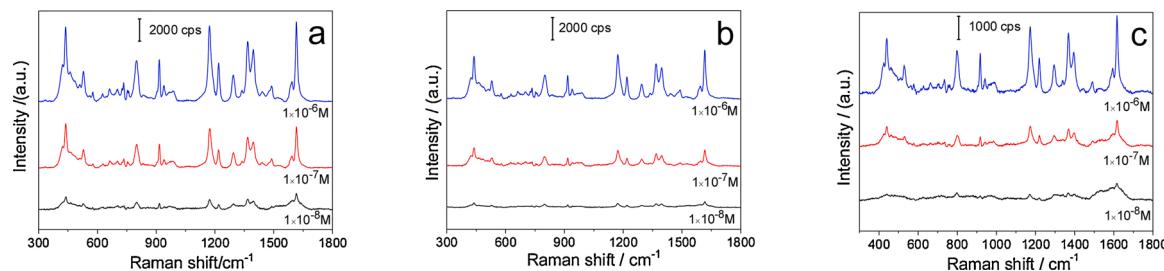
have been reported by many other type Au/Ag-MOF hybrid SERS substrates, such as AgNPs/MIL-101 (30 min), Fe<sub>3</sub>O<sub>4</sub>-Au@MOF (60 min), or Au-MOF (20-140 min) or UAAN@ZIF-8 (10 h) [21,24-27]. While improving the SERS signal, it significantly degrades the detection efficiency. Therefore, a fast detection procedure without sacrificing sensitivity is in great demand.

### 3.4. SERS response in filtration mode

In order to improve the detection efficiency, a new filtration detection mode was developed. In this method, GNU@MOF was assembled onto filter membrane by filtration to form filtration type substrate GNU@MOF-F. Analyte was accumulated onto the substrate by filtration in a short time of 10 s before SERS detection instead of 60 min in immersion mode. Thus, highly efficient detection can be expected. This substrate may combine the advantages of solid phase extraction (SPE) and SERS technology to achieve simple and rapid detection of analyte [35]. We compared the SERS response of the GNU@MOF-F with that of GNU@MOF-I (incubation time 60 min). The results are shown in Fig. 4. Interestingly, the Raman signal of MG on the GNU@MOF-F is comparable or even higher than that on GNU@MOF-I (Fig. 4a), even the interaction time of substrate with analyte is reduced from 60 min to 10 s. When GNU instead of GNU@MOF is coated onto the filter membrane, enhanced SERS signal is also observed on GNU-F compared with that on GNU-I (Fig. 4a). Similar results are also obtained for SERS detection of MB (Fig. 4b). That indicates the filtration induced enhancement has a degree of universality. By combining this filtration based approach with other novel SERS active materials, new advanced SERS substrate can be prepared for practical analysis. Interestingly, such enhancement effect on filtration mode substrate is more obvious for analyte at low concentration level. Fig. 5a,b show the enhancement factor (the intensity ratio of SERS signal on filtration substrate to that on immersion substrate) is about 1.5-fold for 10<sup>-6</sup> M MG, and it increases to 3-fold for 10<sup>-7</sup> and 10<sup>-8</sup> M MG. If the incubation time in the immersion mode was also fixed at 10 s (Fig. 5c), the enhancement factor was further increases to 4.5-fold at 10<sup>-6</sup> M MG, or 7-fold at 10<sup>-7</sup> M and 10<sup>-8</sup> M MG (Fig. 5a,c).



**Fig. 4.** SERS spectra of (a) 10<sup>-5</sup> M MG and (b) 10<sup>-5</sup> M MB on GNU and GNU@MOF in immersion mode (GNU-I and GNU@MOF-I) and filtration mode (GNU-F and GNU@MOF-F).



**Fig. 5.** SERS spectra of 10<sup>-6</sup> - 10<sup>-8</sup> M MG on (a) GNU@MOF-F, (b) GNU@MOF-I (60 min incubation time), and (c) GNU@MOF-I (10 s incubation time).

Based on these results, it is clear the filtration mode can obviously improve the detection efficiency while further amplify the SERS signal compared with the typical immersion mode. The signal enhancement is closely related to the filtration operation. First, filtration improve the enrichment of analyte on the GNU@MOF. By pushing the analyte solution to pass through the filter, nearly all of analytes have high opportunity to interact with substrate and thus more molecules can be accumulated onto the surface of substrate. This can be reflected by UV-vis. Fig. S3 shows the absorption intensity of MG solution decreases after it passes through GNU@MOF-F within 10 s or incubation with GNU@MOF-I for 60 min. The absorption is lower for filtrate passed through the GNU@MOF-F, confirming more analyte molecules are left on substrate. Second, filtration benefits the uniform assembly of GNU@MOF. During filtration operation, the flux pressure can flatten the GNU@MOF on the membrane, make them evenly distributed on the membrane [36], which avoids serious, random aggregation and thus form efficient hotspots [37]. This can be reflected by the SEM images of the GNU@MOF-F substrate. The original filter displays a porous structure. After filtration, the whole filter was covered by GNU@MOFs (Fig. S4a). Further magnified image shows GNU@MOFs are evenly and uniformly distributed onto the filter membrane, leaving almost no large void (Fig. S4b). As a result, plenty of uniform and efficient hot-spots are formed. For immersion detection mode, GNU@MOF is separated and dropped onto silicon slide before detection. In this case, coffee ring and random aggregation of GNU@MOF cannot be avoided [38]. Fig. S4c shows the surface of silicon slice is covered with GNU@MOFs, but further magnified image reveals lots of particles piled up on the surface, leaving large void (Fig. S4d). Therefore, less GNU@MOF can form efficient hot-spots for SERS enhancement compared with that of GNU@MOF-F. Consequently, low signal intensity was observed. This also leads to low signal reproducibility as confirmed in the following section. In a word, the filtration type substrate GNU@MOF-F combines the fast separation, simple operation and high enhancement ability shows great promise for SERS analysis.

### 3.5. Comparison of detection limit and reproducibility

To further test the performance of GNU@MOF-F for SERS analysis, the SERS responses of MG at different concentrations on GNU@MOF-F was recorded. Fig. 6a shows the SERS intensity of MG gradually decreases as the concentration of MG decreases. The lowest detectable concentration is 0.1 nM on this GNU@MOF-F. For comparison, SERS signals of MG on GNU@MOF-I were also tested. The signal of MG at the same concentration is weak compared with that on GNU@MOF-F (Fig. 6b), and the lowest detectable concentration is 1 nM, which is one order of magnitude higher than that on GNU@MOF-F. If 10 s incubation time is used in immersion mode, the detection limit increases to 10 nM (Fig. 5c). This further confirms the advantage of GNU@MOF-F in sensitive analysis. For both substrates, good linear relationship is established for lg[SERS intensity] versus -lg[MG concentration] (Fig. S5), implying a great potential in quantitative analysis. Comparison with other substrates (Tab. S2), the developed GNU@MOF also shows advantages in low detection limit and fast operation.

Besides high sensitivity, signal reproducibility is also an important parameter for a practical SERS substrate. Here, another probe MB is used to estimate the reproducibility of different substrate. Fig. 7a shows the SERS spectra of MB recorded from 10 random sites of GNU@MOF-F substrate. For three typical peaks, the RSD of signal response is between 11.8-12.9% (Fig. 7b). For comparison, the SERS response of MB from GNU@MOF-I were also recorded (Fig. 7c). The corresponding RSD of SERS intensity is 34.2-42.7% (Fig. 7d). The great improved reproducibility for GNU@MOF-F can be ascribed to the filtration pressure. The flux exerts an even pressure onto the GNU@MOF, which avoids serious aggregation and achieves uniform assembly of GNU@MOF on the filter membrane (Fig. S4). For GNU@MOF-I, the substrate material was coated onto silicon wafer, and dried in air. The slow, uncontrolled solvent evaporation and "coffee ring" effect leads to a significant and random aggregation, which leads to poor signal reproducibility (Fig. S4c,d). Although the "coffee ring" effect can be reduced after cleaning silicon wafer by hydrofluoric acid, the process needs professional and

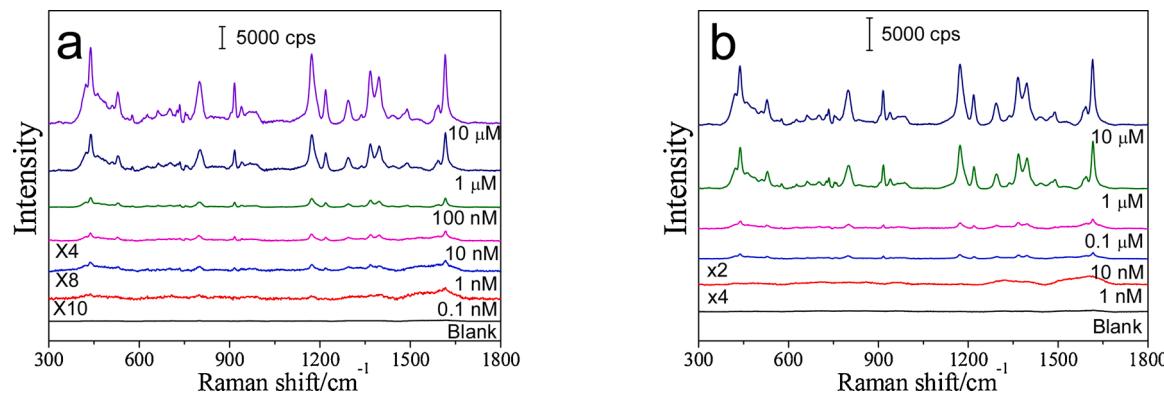


Fig. 6. SERS signals of MG at different concentrations on (a) GNU@MOF-F, (b) GNU@MOF-I.

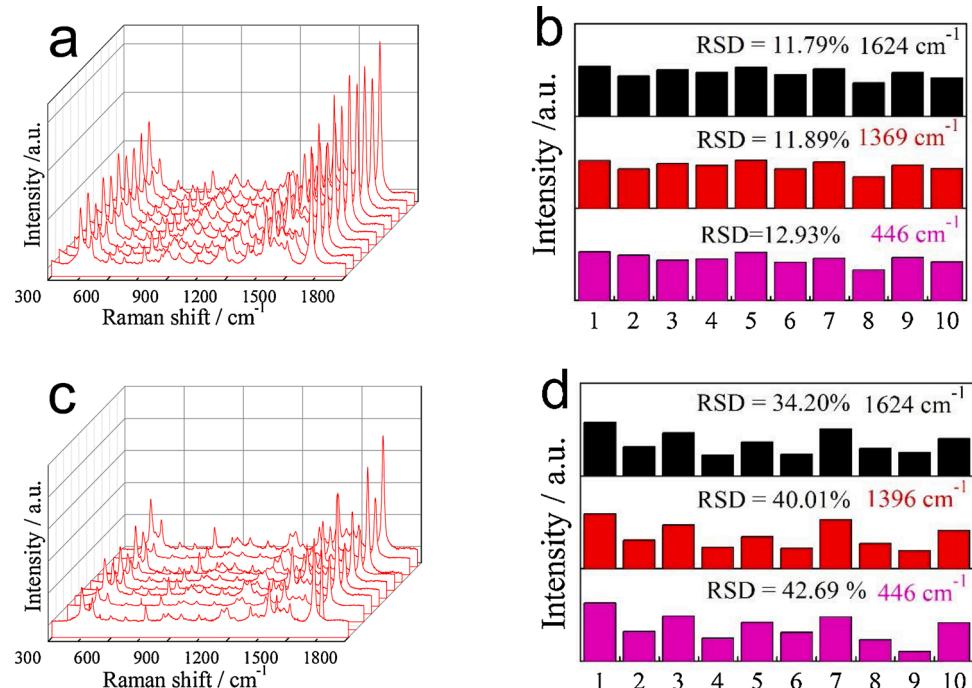


Fig. 7. SERS spectrum of MB obtained from 10 random sites on (a) GNU@MOF-F, and (c) GNU@MOF-I, and corresponding RSD values for peak intensity at 446, 1369 and 1624 cm<sup>-1</sup> for (b) GNU@MOF-F (b) and GNU@MOF-I (d).

careful operations, which is tedious and dangerous. Therefore, the filtration mode substrate not only enhance sensitivity, but also improves signal reproducibility and detection efficiency.

### 3.6. Real sample analysis and substrate reusability

Due to the high enhancement ability, good reproducibility and short

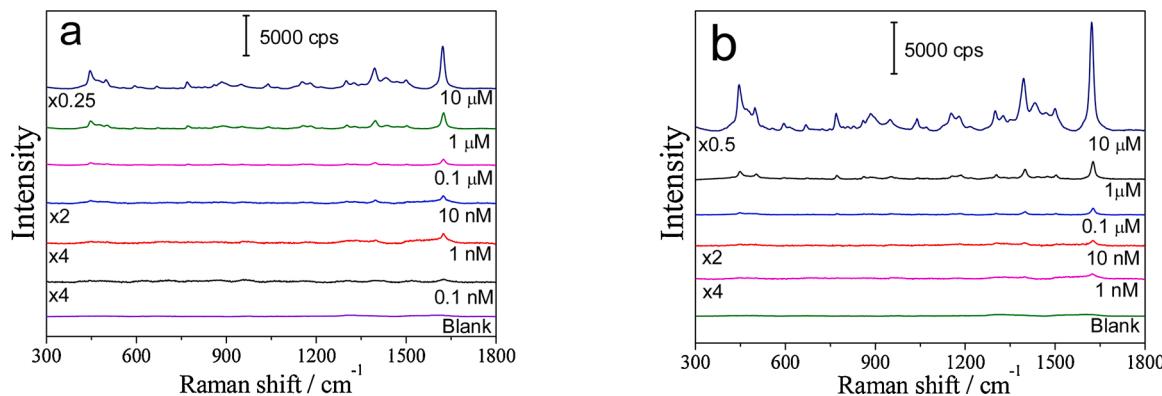


Fig. 8. SERS response of MB spiked in lake water using (a) GNU@MOF-F or (b)GNU@MOF-I as enhancement substrate.

detection time, the potential application of GNU@MIL-100(Cu) for real sample analysis was investigated. Methylene blue (MB) belongs to thiazide dyes. It can be used to treat central nervous system diseases and used as a disinfectant in aquaculture. However, high concentrations of MB can cause animal poisoning or death, red blood cell morphology changes and other symptoms [39]. Therefore, a simple and efficient method to detect MB is important to control its use within a safe range. Here, GNU@MOF-F is used as the substrate for SERS detection of MB spiked in local lake water to evaluate its practical application. In Fig. 8 (a), the characteristic peaks of MB at 446, 503, 1396 and 1624 cm<sup>-1</sup> can be clearly recognized (band assignment can be found in Table S1). As the concentration of MB decreases, the SERS signal also gradually decreases. When the concentration is reduced to 10<sup>-10</sup> M, we can still observe multiple characteristic peaks of MB. Thus, the lowest detectable concentration is 0.1 nM. For comparison, GNU@MOF-I with 60 min incubation time is also used to detect MB. The characteristic peaks of MB can be seen when the concentration of MB is in the range of 10<sup>-6</sup> M to 10<sup>-9</sup> M. The lowest detectable concentration on GNU@MOF-I is also one order of magnitude higher than that on GNU@MOF-F, further confirming the advantage of coating GNU@MOF onto filter. Good linear relationships were established for lg[SERS intensity] versus -lg[MB concentration] for both substrates (Fig. S6 in SI). The GNU@MOF-F is also used to detect thiram in lake water (Fig. S7), and the performance is better than some reports (Table S1). All these results indicate GNU@MOF-F has great promise in practical analysis.

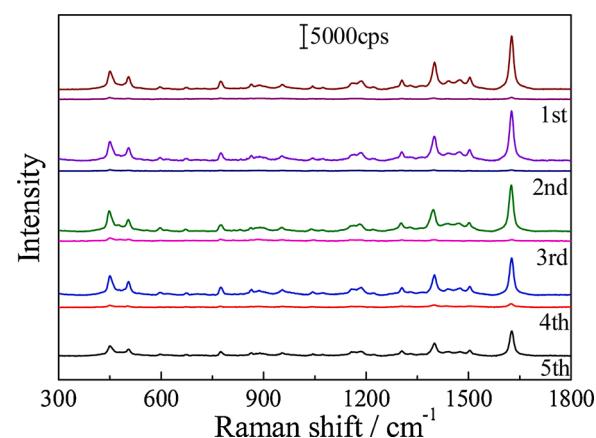
Reducing the cost of substrates is also important for practical analysis. SERS substrate with a degree of reusability is an alternative to reduce the cost. Here, the reusability of the GNU@MOF-F is investigated. As shown in Fig. 9, the newly prepared GNU@MOF-F presents strong SERS signal for MB. The organic filter was washed several times with absolute ethanol, and SERS response was recorded again. It is found the SERS signal of MB almost disappears. Then, MB solution was passed through the filter again. The Raman signal of the MB molecule appears again, and its intensity almost the same to that of the first time. After three cycles of test, there is no significant change in the SERS signal of the MB. After that, a 40% decrease in signal intensity is observed, which is caused by the aggregation of GNU@MOF induced by the fast injection operation (Fig. S8). Therefore, the GNU@MOF-F substrate can be reused for at least 3 cycles. Besides, the shelf-life study indicates the substrate can be used within 16 days without obvious signal attenuation (Fig. S9).

#### 4. Conclusions

Gold nano-urchin wrapped with metal organic framework MIL-100 (Cu) was assembled onto filter membrane to form a new filtration type SERS substrate GNU@MOF-F. The substrate with dense and uniform hot-spots can achieve fast and sensitive SERS molecule sensing within 1 min by simple filtration, which shows higher SERS signal, lower detection limit, improved reproducibility and higher efficiency than traditional immersion method for molecule sensing. For practical application, the GNU@MOF-F was used to detect toxic MB in lake water and the lowest detectable concentration is 0.1 nM. Finally, the GNU@MOF-F substrate also shows proper reusability. The GNU@MOF-F with simple and fast operation should have promising application in environmental detection, food safety and so on.

#### CRediT authorship contribution statement

**Fugang Xu:** Conceptualization, Project administration, Writing - review & editing, Methodology. **Wenjuan Shang:** Investigation, Formal analysis, Writing - original draft. **Guangran Ma:** Software, Writing - review & editing. **Yongmei Zhu:** Data curation. **Meijuan Wu:** Formal analysis.



**Fig. 9.** SERS signal of MB obtained on GNU@MOF-F during different cycles of detection-wash operation.

#### Declaration of Competing Interest

The authors report no declarations of interest.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.snb.2020.128968>.

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