Ultra-rapid and highly efficient enrichment of organic pollutants via magnetic nanoparticles/mesoporous nanosponge compounds for ultrasensitive nanosensors

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Abstract

Developing advanced sensing and detection technologies to effectively monitor organic micropollutants in water is under urgent demand in both scientific and industrial communities. Currently, owing to the ultrahigh sensitivity on the single-molecule level with highly informative spectra characteristics, SERS technique is regarded as the most direct and effective detection technique. However, some weakly adsorbed molecules, such as most of persistent organic pollutants, cannot exhibit strong SERS signals, which is a long-standing key challenge that has not been solved. Here, we show an enrichment-typed sensing strategy based on a powerful porous composite material, call mesoporous nanosponge. The nanosponge consists of magnetic nanoparticles immobilized porous β-cyclodextrin polymers, demonstrating remarkable capability of effective and fast removal of organic micropollutants, e.g. ~90% removal efficiency within ~1 min. With the anchoring of magnetic nanoparticles, the current new polymer adsorbent can be easily recycled from water and re-dispersed in ethanol so that the target molecules in the cavity of adsorbent is concentrated, with an enrichment factor up to ~103. By means of the current enrichment strategy, the limit of detection (LOD) of the typical organic pollutants can be significantly improved, i.e. increasing 2~3 orders of magnitude, compared with the detection without molecule enrichment protocol. Consequently, the current enrichment strategy is proved to be applicable in a variety of fields for portable and fast detection, such as Raman and fluorescent.

Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs) was endorsed by 131 nations in 2004 to eliminate most persistent bioaccumulative and toxic substances in the world. Organic micropollutants of ground and surface water resources, such as pesticides and plastic components, have aroused great concerns about potential negative effects on aquatic ecosystems and human health. Therefore, parallel to the researches of adsorbent materials to remove organic pollutants from water, the ultrasensitive detection of organic pollutants is another crucial field, since the solubility of organic micropollutants in water is always at the trace level. Among diverse detection approaches, surface-enhanced Raman scattering (SERS), which achieved significant breakthroughs in 1997 and became the first vibrational spectroscopy technique that could provide delicate information on molecular fingerprints with potential single-molecule level of sensitivity, is regarded as the most simple, fast, flexible and portable detection technique.

However, up to date, the superiority of single-molecule SERS in the detection of diverse molecules with intrinsic small cross-sections or low affinity for the plasmonic surface has not been into full play, particularly in real complex situation. As is well known, the SERS process involves complicated coupled three-body interactions among photons, molecules, and nanostructures. Besides the interaction between light and nanostructures, the investigation on the interaction between molecule and plasmonic surface is of importance. On the one hand, SERS is an optical near-field effect. A high activity can be obtained only when the target molecule is very close to the plasmonic surface. On the other hand,
most organic pollutants in water can not be effectively adsorbed onto a metallic surface because of their low affinity toward the metal. Therefore, recently, some strategies, such as selective enrichment and spatial localization of target molecules, are suggested to solve this long-standing challenge.

In this work, we propose a new sensing strategy based on the efficient enrichment and rapid separation of POPs by means of the magnetic nanoparticles immobilized porous β-CD polymer (MN-PCDP), called mesoporous nanosponge. The microporous β-cyclodextrin (β-CD) material, an inexpensive and renewable carbohydrate, which is featured by small pores and high surface areas, was used in this work as an excellent adsorbent. In fact, microporous β-CD material has been widely studied because of outstanding adsorption efficiency through forming host-guest inclusion with many hydrophobic organic pollutants. The magnetic nanoparticles are introduced into the MN-PCDP compounds to rapidly separate the adsorbent from water. The current strategy (the schematic description of the protocol is shown in Fig. 1) demonstrates several remarkable advantages. Firstly, as shown in Fig. 1a, when the MN-PCDP adsorbent (shown in Fig. 1b) is dispersed into water in the beaker, e.g. ~1000 ml, containing organic pollutants, ultra-rapid adsorption and magnetic separation can be accomplished, i.e., totally within ~ 1 min. Secondly, the adsorbed pollutant in MN-PCDP from water can be desorbed in ethanol with a volume of ~1 ml, for further analysis such as UV-vis, Raman and fluorescent spectroscopy. Thus, an ultra-high enrichment efficiency with an enrichment factor up to ~10³ times can be obtained (Fig. 1c). With current enrichment strategy, the limit of detection (LOD) in a variety of sensing applications, such as SERS and fluorescent, can be lowered by 2~3 orders of magnitude. Furthermore, through the magnetic separation, the MN-PCDP mesoporous nanosponge can selectively adsorb the target organic pollutants, avoiding the disturbance of complex matrix. The current sensing strategy can be believed to be applicable to a wider range of sensing areas for an economical, simple, fast, flexible, and portable detection.

Results

Synthesis and characterization. The MN-PCDP was prepared by cross-linking polymerization of β-CD and cross-linking agent (tetrafluoroterephthalonitrile (TFT)), with magnetic nanoparticles (Fe₃O₄) in one-step solvothermal reaction. Fig. 2a-c show the transmission electron microscope (TEM) images of magnetic nanoparticles (MN, Fe₃O₄), porous β-CD polymer (PCDP) and MN-PCDP, respectively. As shown in Fig. 2a, the synthesized MN exhibits regular spheres with good dispersibility and uniform size (average size ~200 nm). The Fourier transform-infrared spectroscopy (FT-IR) spectrum of MN is displayed in Fig. 2d. The absorption bands at 1652 cm⁻¹ and 1396 cm⁻¹ of the MN can be associated with carboxylate group and that also appear in the MN-PCDP. Fig. 2b and Supplementary Fig. 1 exhibit that the PCDP is porous network structure. After the immobilization of MN, as shown in Fig. 2c, the porous network structure of MN-PCDP is not disrupted. The FT-IR spectrum of the MN-PCDP not only obviously combines the characteristic peaks of the TFT and the β-CD but also displays a new peak at 1265 cm⁻¹ in relation to the newly formed C-F group, implying that the β-CD has been crosslinked with TFT. Fig. 2e indicates that the Brunauer-Emmett-Teller surface areas ($S_{BET}$) of MN-PCDP is about 66 m² g⁻¹. The pores with diameter
of 1.7-3.0 nm comprise the majority of the free volume of MN-PCDP and its average pore diameter is 2.12 nm.

**Adsorption of MN-PCDP nanosponges.** The high surface area and permanent porosity of MN-PCDP mesoporous nanosponge enable the rapid removal of organic micropollutants from water.\(^{25}\) As shown in Supplementary Fig. 2, the PCDP and MN-PCDP displays the same properties in time-dependent adsorptions of bisphenol A (BPA), illustrating the immobilization of magnetic nanoparticles has no remarkable influence on the adsorption performance of PCDP. The time-dependent adsorptions of various organic micropollutants adsorbed by MN-PCDP, including plastic components, pesticide and aromatic model compounds (Fig. 3a), are shown in Fig. 3b, Supplementary Fig. 3 and Supplementary Table S1. The removal rate of the above organic micropollutants is very fast, which tends to be constant within 1 min. The removal efficiencies of BPA, parathion, carbendazim and 2-naphthol (2-NO) are more than 80% in 30 sec, which is much higher than the Norit ROW 0.8 supra extruded activated carbon (NAC) as presented in Fig. 3c, Supplementary Fig. 4-5 and Supplementary Table S2. We further probe the readily accessible binding sites of MN-PCDP by determining the flow-through uptake of different organic micropollutants. In these experiments, the adsorbent (~5 mg) was trapped as a thin layer on a 0.22 μm syringe filter, and aqueous organic pollutants (5 ml, 0.1 mM) passed rapidly through the filter at a flow rate of 10 ml min\(^{-1}\) (Supplementary Fig. 6). Under these conditions, for example, 76% of the BPA is removed from the solution, corresponding to more than 84% of its equilibrium adsorption, confirming that the host-guest interaction plays a major role in the filtration process by syringe.\(^{26}\) The superior performance of MN-PCDP can be further indicated that its β-CD moieties are easily accessed by most of organic micropollutants. Furthermore, these molecules are rapidly trapped. In addition, the influence of the concentrations of adsorbent on the BPA adsorption efficiency is studied as shown in Fig. 4b, Supplementary Fig. 7 and Supplementary Table S3. When the concentration of adsorbent increases from 0.1 mg L\(^{-1}\) to 1.0 mg L\(^{-1}\), the adsorption efficiency of BPA is enhanced from 25.12% to 87.09% within 1 min and from 35.07% to 89.82% within 10 min.

**Desorption and enrichment of MN-PCDP nanosponges.** As we all know, organic micropollutants exhibit good solubility in organic solution, such as ethanol and methanol.\(^{18}\) Hence, after adsorption process, we utilized ethanol to desorb the organic micropollutants from MN-PCDP mesoporous nanosponges, and then obtained the enriched pollutant solution through magnetic nanoparticle separation. In order to obtain higher concentration of desorbed micropollutant solution, in this work, we chose 1 mL ethanol to desorb organic micropollutants adsorbed in 100 mg MN-PCDP adsorbent. As shown in Supplementary Fig. 8, using current enrichment processes, the concentration of BPA can be increased to 88.5 times of its initial concentration with a recipe of 100 mL organic pollutant (BPA) solution and 100 mg MN-PCDP adsorbent. This result reveals that more than 98% of the adsorbed organic micropollutants are desorbed into the ethanol solution. That is to say, for 100 mL organic pollutant solution, we realize ~10\(^2\) times enrichment of target molecule. As the amount of adsorbent increases, the adsorption efficiency tends to reach equilibrium. Considering the cost increase of sample preparation and the operation in the
desorption process (with 1 mL ethanol) resulting from the increase of adsorbent dosage, 100 mg of adsorbent is selected as the amount of material for subsequent experiments.

In order to further improve the enrichment effect of 100 mg adsorbent in total 1000 mL organic micropollutants, herein, we attempted three methods, including 100 mL×10 times, 250 mL×4 times and 500 mL×2 times, to optimize the adsorption and desorption processes. Importantly, the adsorbent can be simply separated by magnet in every adsorption cycle, and desorbed in ethanol in the last adsorption cycle. As shown in Fig. 4c, Supplementary Fig. 9 and Supplementary Table S4, with adsorption times increasing, the removal efficiencies of these three methods gradually decrease. The removal efficiencies of these three methods (100 mL×10 times, 250 mL×4 times and 500 mL×2 times) are 50.78%, 62.58% and 41.22%, respectively. Meanwhile, the enrichment efficiencies of these three methods are 485, 605 and 396 times of the initial concentration (Fig. 4d), respectively. Therefore, we achieve over 600 times’ enrichment of organic pollutants (with 1000 mL of initial micropollutants) in the optimized adsorption and desorption processes. Here, the selected parameters (100 mg adsorbent in 250 mL organic solution for 4 cycle times) were used for the succedent experiments. Meanwhile, it is also worth noting that the separation process by magnet is very fast and facile, such as 90 sec for 250 mL solution (Fig. 4a and Supplementary Fig. 10b), 60 sec for 100 mL (Supplementary Fig. 10a), and 150 sec for in 500 mL (Supplementary Fig. 10c), fully meeting the requirement of immediate-pretreatment detection application.

**SERS and fluorescence measurement of pollutants based on the enrichment of MN-PCDP nanosponges.**

Many POPs are mutagenic, carcinogenic and not degradable by direct biological treatment, some of which damage nerve, endocrine systems of human body, and the ecological balance due to their toxicity in nature. Based on the above experimental researches, the MN-PCDP nanosponges were used to absorb organic micropollutants and then were collected from water (Fig. 5a), so as to realize the rapid removal and enrichment of POPs. Moreover, we evaluated fluorescence and enhanced Raman spectra of POPs (carbendazim and BPA) to demonstrate the enrichment effect of current enrichment strategy. The enhanced Raman spectra of carbendazim molecular with ~55 nm Au nanoparticles (Supplementary Fig. 11) were measured under 785 nm laser. As shown in Figure 5b-c, without the enrichment process, the LOD of SERS for carbendazim is 1 nM, but after the enrichment using MN-PCDP adsorbent, this value reaches to ~5 pM, which shows an increase of $10^2 \sim 10^3$. In Supplementary Fig. 12, for BPA molecule, with the help of adsorbent, the LOD of fluorescence is also greatly improved. In Fig. 5d-e and Supplementary Fig. 13, based on the current enrichment sensing strategy, the LODs of fluorescence detections for the pure solution of carbendazim and BPA are lower by 2~3 orders of magnitude. In this study, the enrichment strategy based on the adsorption and desorption processes of MN-PCDP adsorbent may significantly increase the sensitivity of plasmonic sensors, compared with the LOD for similar molecules, illustrating its wide applicability.

Owing to the excellent enrichment and easily-separated features, the current strategy was believed that the mesoporous nanosponges could be served as a preprocessing for direct, rapid and ultrasensitive detection of contaminants in complex situations. After adsorption process, the MN-PCDP adsorbent was easily collected on the wall of beaker (Fig. 5a) with a magnet, avoiding the interference of complex
matrix, such as mud and microorganism. Fig. 5f reveals that both the characteristic peaks of BPA (830 and 1179 cm\(^{-1}\)) and carbendazim (1008, 1244 and 1263 cm\(^{-1}\)) evidently appear in the Raman spectrum of mixture solution, including 1 µM BPA and 10 nM carbendazim. Furthermore, the MN-PCDP demonstrates a superior reusability as shown in Supplementary Fig. 14. Six consecutive BPA adsorption/desorption cycles were performed and the regenerated MN-PCDP exhibited almost no decrease (90.2% to 87.5%) in performance compared to the as-synthesized polymer.

**Discussion**

In summary, we have developed a robust and rapid sensing strategy based on the MN-PCDP mesoporous nanoponges to capture and enrich organic pollutants from water. In this strategy, the MN-PCDP adsorbent exhibits excellent adsorption capacity for various kinds of pollutants owing to the unique cavity structures. Moreover, the adsorbed pollutant in MN-PCDP can be desorbed in ethanol with a very fast and facile operation. In SERS detection of organic pollutants, i.e. carbendazim and BPA, in this work, the current sensing strategy may significantly increase the sensitivity of plasmonic sensors with 2~3 orders of magnitude. Therefore, the current robust sensing strategy with the ultra-rapid and highly efficient sample pretreatment and molecule enrichment is believed to be applicable to a wider range of sensing devices, such as fluorescent, Raman and infrared spectroscopes for a cost-effective, simple, fast, flexible and portable detection.

**Methods**

**Preparation of magnetite nanoparticles (Fe\(_3\)O\(_4\)).** The carboxyl-functionalized magnetite nanoparticles (Fe\(_3\)O\(_4\)) with highly water-dispersibility were synthesized by a modified solvothermal reaction approach. Typically, FeCl\(_3\)·6H\(_2\)O (1.08 g, 4.0 mmol) and trisodium citrate (0.20 g, 0.68 mmol) were dissolved in ethylene glycol (20 mL) with stirring at 500 rpm. Afterward, sodium acetate trihydrate (2.0 g, 15 mmol) was added and the mixture was stirred for 30 min. Then, the mixture was sealed in a Teon-lined stainless-steel autoclave (50 mL). The autoclave was heated at 200 °C for 12 h, and then allowed to cool to room temperature. The black products were washed with ethanol and ultrapure water for several times. Finally, the carboxyl-functionalized magnetite nanoparticles (Fe\(_3\)O\(_4\)) were separated by magnet, redispersed in ethanol and dried in vacuum drying oven at 30°C.

**Preparation of magnetic nanoparticles immobilized porous β-CD polymer (MN-PCDP).** The MN-PCDP composites were then prepared by modification of nucleophilic aromatic substitution method of hydroxyl groups of β-CD. A dried 100 mL Shrek reaction vial with a magnetic stir bar was charged with β-CD (0.82 g, 0.724 mmol), TFT (0.40 g, 1.03 mmol), and K\(_2\)CO\(_3\) (1.28 g, 9.28 mmol) and dried Fe\(_3\)O\(_4\) (0.041 g). The vial was flushed with N\(_2\) gas for 10 min, then an anhydrous THF/DMF mixture (9:1 v/v, 40 mL) was added and the vial was purged with N\(_2\) for additional 5 min. After that, the N\(_2\) inlet was removed. The mixture was stirred at 500 rpm and refluxed at 85°C for 36 h under nitrogen protection. The brown suspension was cooled to room temperature and magnetically separated the supernatant by magnet. The
precipitate was washed twice with an appropriate amount of distilled water, THF, ethanol and CH$_2$Cl$_2$, respectively. The final precipitate was vacuum dried at 77 K in a liquid nitrogen bath for 24 h and then the magnetic nanoparticles immobilized porous β-CD polymer (MN-PCDP) was obtained.

**Batch adsorption kinetic studies.** In studies, the dried polymer (MN-PCDP, 20 mg) was initially washed with H$_2$O for 2 times and then separated by magnet. Adsorption kinetic studies for different pollutants were performed in 30 mL scintillation vials with 20 mL organic pollutant solution and 20 mg adsorbent, at ambient temperature on a hot plate at 25°C. Then the sample was shaken at 250 rpm until the adsorption equilibrium was reached. The mixture was immediately stirred and 1 mL aliquots of the suspension were taken at certain intervals via syringe and filtered immediately by a 0.22 μm PTFE membrane filter. The residual concentration of the pollutant in each sample was determined by UV–vis spectroscopy.

**Calculation of removal efficiency.** The removal efficiency of pollutant removal by the adsorbent was determined by the following equation:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

where $C_0$ and $C_t$ are the initial and residual concentration of pollutant in the stock solution and filtrate, respectively.

**Flow-through adsorption experiments.** Individual pollutants were at high concentrations (mM). 5.0 mg of the MN-PCDP adsorbent was washed with deionized H$_2$O for 2 times, then the precipitate was pushed by a syringe through a 0.22 μm PTFE membrane filter to form a thin layer of the adsorbent on the filter membrane. 5 mL of the pollutant stock solution was then pushed through the adsorbent in ~30 s (10 mL min$^{-1}$ flow rate). The filtrate was then measured by UV–vis spectroscopy to determine the pollutant removal efficiency.

**MN-PCDP desorption studies.** 100.0 mg of the adsorbent was washed with deionized H$_2$O for 2 times, and then added to the organic pollutant stock solution (0.01 mM) with determine volume (100 mL, 250 mL, 500 mL). The mixture was shaken at 250 rpm for 1 min at 25°C. After separating the supernatant and the adsorbent by an external magnet, the supernatant was filtered through a 0.22 μm filter membrane and determined by UV-vis spectroscopy. Meanwhile the precipitate was evaporated to dryness with a gentle nitrogen stream, then the residue was dissolved in 1mL of ethanol to desorb the adsorbed organic pollutant. The desorption solution was measured by UV-vis spectroscopy and compared with the initial concentration of pollutant in the stock solution.

**Calculation of enrichment efficiency.** The enrichment efficiency of pollutant adsorbed by the adsorbent was determined by the following equation:
Where $C_0$ and $C$ are the initial and desorbed solution concentration of pollutant, respectively.

**Fluorescence measurement.** The fluorescence spectra of pure solution were directly measured by fluorescence spectrophotometer.

**Preparation of SERS active Au NPs.** The Au NPs with different size in diameter were synthesized based on a modified citrate reduction approach. The growth process of gold nanoparticles with different size included three steps. For step 1, 100 mL of ultrapure water was added into a conical flask and heated to boiling. Then, 4 mL of 1 wt% sodium citrate (SC) solution was injected immediately, and 3.2 mL of 10 mM HAuCl$_4$ was added after 3 min. Kept the reaction for 25 minutes and made it natural cooling, then the Au seeds were obtained. For step 2, 80 mL of ultrapure water and 20 mL of Au seeds were mixed into the conical flask and heated to boiling. Then, 2 mL of 1 wt% sodium citrate solution was injected immediately, and 0.2 mL of HAuCl$_4$ was added 3 min later. Then additional 0.2 mL × 9 dosage of HAuCl$_4$ was injected every 8 minutes. After the last precursor was added, the reaction was kept for 25 min, and Au NPs-25 nm were obtained. For step 3, Au NPs prepared in step 2 were used as the seed solution, and the growth process was repeated as growth steps 2, and then Au NPs-55 nm were obtained in this step.

**SERS measurement.** SERS measurement is based on the hydrophobic slippery surface. Concentrated molecules and Au NPs were prepared on a hydrophobic slippery Teon membrane as follows: First, a Teon membrane was attached on a flat glass slide (5 cm × 5 cm) by using a double-sided adhesive. Then, 0.5 mL of perfluorinated fluid was dispersed by spin coating. The low speed was 300 rpm for 30 s, and the high speed was 1500 rpm for 1 min. After the excess lubricating liquid was removed by centrifugal force, and the infused membrane was heated for 30 min. Lastly, 50 μL of probe molecules and 10 μL of Au colloids were simultaneously dropped onto the slippery surface. During drying, the contact line shrunk because of the low friction of the lubricated Teflon surface. As a result, the initial droplet could be concentrated into a small area less than 0.5 mm in diameter.

**Declarations**

**Data availability**

The data that support the findings of this study are available within the paper and its Supplementary Information or from the corresponding authors on reasonable request.

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**Author contributions**

L.L.Z. synthesized the materials, carried out the characterizations and performance, analyzed the data, and wrote the manuscript. R. H., H. N., Y. Z. D. contributed in part of the TEM, Raman and fluorescence characterizations. H.J.Y. and J.X.F., supervised the project, designed the experiments, contributed in discussions, comments and writing of manuscript. All authors discussed the results and commented on the manuscript.

**Additional information**

Supplementary Information accompanies this paper at

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Figures
Figure 2

Characterizations of magnetic nanoparticle (MN), porous β-CD polymer (PCDP) and magnetic nanoparticles immobilized porous β-CD polymer (MN-PCDP). TEM images of a MN, b PCDP, and c MN-PCDP. d FT-IR spectra of MN (black), TFT (red), β-CD (blue), PCDP (orange) and MN-PCDP (green). e N2 adsorption isotherms and cumulative pore volume of MN-PCDP.