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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Au nanoparticle-incorporated sponge as a versatile transmission surface-enhanced Raman scattering substrate

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

We report a sponge-based transmission surface-enhanced Raman scattering (TSERS) substrate that combines the bulk sampling capabilities of a transmission measurement able to improve the quantitative representation of sample concentration with several sponge properties useful for analysis such as fast sample uptake, easy sample enrichment, and a stable polymeric structure. Among nine commercially available sponges made of different materials, a melamine sponge was ultimately selected for this study because it provided the fastest sample uptake and a low background Raman signal. Simultaneously, the amino groups and three-nitrogen hybrid rings in its structure could easily hold Au nanoparticles (AuNPs) inside the sponge. AuNP-incorporated sponges (AuNP sponges) were prepared by simply soaking a melamine sponge in a AuNP solution; these sponges were initially used to measure 4-nitrobenzenethiol (4-NBT) samples with different concentrations in order to evaluate their ability as TSERS substrates. The intensities of the 4-NBT peaks clearly varied according to changes in the concentration, and the relative standard deviation (RSD) of the peak intensity estimated by the measurements of five independently prepared AuNP sponges was 10.0 %. Sample enrichment was easily completed by repeated suctioning of the sample into the AuNP sponges followed by depletion of the solvent, so three-time enrichment doubled the intensity. Furthermore, paraquat samples were prepared in diverse matrices (de-ionized water, tap water, river water, and orange juice) and measured using the AuNP sponges. The paraquat peaks were clearly observed from these samples and their peak intensities became smaller with the increased compositional complexity of the matrices. Our overall results demonstrate that the TSERS substrates are easy to prepare and practically versatile for SERS analysis of diverse samples.

Introduction

Recently, transmission Raman spectroscopy (TRS) has emerged as an effective method for diminishing sub-sampling problems that frequently occur during Raman measurement of non-homogeneous samples; sample representation is improved by the deep bulk-sampling capabilities of this method.[1-4] Measurements based on TRS are accomplished via laser illumination through a sample and the subsequent collection of the transmitted Raman photons. This allows the diffused laser photons to interact globally with a sample; therefore, the acquired transmission spectrum is much more representative of the whole composition of the sample, especially when internal compositional heterogeneity is present.[4] Due to the utility of the transmission Raman measurement, it has been readily applied for the analysis of diverse samples in agricultural and pharmaceutical fields.[4-8]

Meanwhile, surface-enhanced Raman scattering (SERS) is a valuable phenomenon that can be used to overcome the inherent low sensitivity of Raman-based quantitative analyses; therefore, widely different SERS substrates, such as nanoparticles, nanorods, nanodendrites, and regularly-patterned surfaces, have been developed for diverse analytical detection and bio-imaging.[9-15] SERS is a highly localized event and the intensity of a sample is dependent on where the sample molecule is positioned on a SERS substrate.[16] This is a critical issue that directly influences the reliability of SERS-based quantitative analysis.[17] One typically practiced approach used to acquire SERS spectra with superior quantitative representation is the use of an averaged spectrum; this is done by averaging the spectra collected at multiple spots on a substrate. However, determining the number of spectral collection spots used for averaging is highly subjective and increases the overall analysis time.

One reliable and alternative approach could be the use of a scheme that provides simultaneous bulk Raman sampling covering the whole (or nearly the whole) volume of a SERS substrate for spectral acquisition. In this way, varying Raman intensities of a sample generated from different spots on a SERS substrate can be leveraged and the overall intensity becomes more quantitatively representative. For this reason, a substrate that enables the transmission SERS (TSERS) measurement is beneficial for quantitative analysis; however, studies on TSERS substrates have rarely been reported. There are two major requirements for a TSERS substrate. First, it is necessary to hold SERS-generating nanostructures internally without serious leakage during analysis and quickly introduce the sample inside of it for fast analysis. Second, the substrate must produce a reasonable amount of photon diffusion in order to widely interact with the internally-housed SERS materials for bulk sampling. While, a high degree of diffusion diminishes the number of photons crossing a substrate and thus decreases the transmission Raman signal. In addition, the preparation of a substrate needs to be simple and the substrate material is easily obtainable.

In this publication, we have reported a sponge-based TSERS substrate and evaluated its analytical performance. The selection of a sponge as the nanostructure-holding three-dimensional (3D) TSERS substrate was to utilize its porous structure in order to generate an adequate amount of photon diffusion inside for bulk interaction with a sample and introduce the sample solution rapidly via simple soaking. The easy availability of the sponge was also an attractive factor for the choice of material. Initially, nine commercially available sponges, made of polyurethane (PU), polyester (PE), melamine (formaldehyde-melamine-sodium bisulfite copolymer), polyvinyl alcohol (PVA), natural pulp, and synthetic rubber, were screened to choose the optimal sponge by evaluating several parameters such as their

water soaking ability, magnitude of their background Raman signal, and nanostructure holding ability. As a result of our evaluation, a melamine sponge was selected and a Au nanoparticles (AuNPs) solution was simply soaked into it for the preparation of a TSERS substrate. Using the TSERS substrate, different concentrations of 4-nitrobenzenethiol (4-NBT) solutions were measured and their intensity variations according to the concentration changes were examined. Finally, paraquat (N,N'-dimethyl-4,4'-bipyridinium dichloride, a popular herbicide) solutions, prepared in diverse matrices (de-ionized water, tap water, river water, and orange juice), were measured to demonstrate the practical applicability of the TSERS substrate.

Experimental section

Preparation of AuNP-incorporated sponges

All reagents used in this study were of the highest available grade, purchased from Sigma-Aldrich, and used as-received. The citrate reduction method was used to initially synthesize seed AuNPs with a diameter of ~15 nm.[18] The average size was 16.2 ± 2.1 nm with the maximum extinction at 520 nm (concentration: 8.43×10^{12} particles/mL). The larger AuNPs (~60 nm) were prepared by the seed-mediated growth method.[19,20] The synthesized seed AuNPs were grown into larger particles by the surface-catalyzed reduction of Au^{3+} by NH_2OH. The average size of the grown AuNPs was 66.1 ± 10.3 nm with the maximum extinction at 537 nm (concentration: 4.82×10^{10} particles/mL).

Nine different sponges made of PU, PE, PVA, melamine (manufactured by BASF), natural pulp, and synthetic rubber were purchased at a local market and are shown in Figure 1. Each sponge was cut into a cube ($1 \times 1 \times 1$ cm^3) with a razor for the screening test. All of the sponges were used as-purchased without further chemical modification. AuNP-incorporated sponges (AuNP sponges) were prepared by simply soaking the cube sponges in the prepared AuNP solution over one minute.

Transmission SERS (TSERS) measurements

To acquire TSERS spectra using AuNP-incorporated sponges, 4-nitrobenzenethiol (4-NBT) was used as a SERS reporter. The prepared AuNP sponges were initially dipped into a 4 μM 4-NBT solution, and then the soaked aqueous solvent was drained by gently dabbing with a water absorbing tissue. The 4-NBT-captured AuNP sponges (referred to as 4-NBT-AuNP sponges) were dried in an ambient environment for TSERS measurement. TSERS spectra were collected by direct illumination of laser radiation (785 nm, Invictus, Kaiser Optical Inc., Ann Arbor, MI, USA) onto the 4-NBT-AuNP sponges (exposure time: 10 s, 1 scan). The laser power at the illumination was 200 mW. Transmitted SERS signals were collected at the opposite of the illumination using a wide area illumination (WAI) scheme (PhAT system, Kaiser Optical Inc.).[21,22] For microscopic investigation of the SERS signal generated from the 4-NBT-AuNP sponge, Raman mapping was performed over one face of the sponge substrate (coverage area: 8.5×8.5 mm^2, mapping interval: 150 μm) using a Raman microscope (Kaiser Optical System). The laser beam was 20 μm in diameter and the Raman spectra were acquired at each mapping point with an exposure time of 1 s. To prepare the paraquat samples in different matrices, river water was obtained from the Han River (Seoul, Korea) and orange juice was purchased from a local store.

Results and discussion

Selection of an optimal sponge for TSERS measurement

Since a diverse range of sponges are commercially available, it was necessary to choose an optimal sponge to meet the requirements of the TSERS substrate. In this study, three types of PU sponges, two types of PE sponges, a melamine sponge, a PVA sponge, a natural pulp sponge, and a synthetic rubber sponge (a total of nine different sponges) were prepared as shown in Fig. 1, and an optimal sponge was found by simultaneously considering several important parameters such as their water soaking ability, magnitude of the background Raman signal, and nanostructure holding ability. The images in the first column in Fig. 1 show the actual appearances of the tested sponges. The volumes of the sponges are approximately 2.0 - 2.5 cm^3. To highlight the two-dimensional appearance of the sponges, a thin slice was prepared from each sponge and their top-view images were acquired, as shown in the second column. Each image covers an area of ~1.0 × 1.0 cm^2 of the sliced sponge. The images in the third column are the corresponding enlarged images with 40-fold magnification. The structures, pore sizes, colors, and textures are all different from one another.

To screen the sponges, the water soaking time, which is directly related to analysis time, was the first tested parameter. For this purpose, each 1 cm^3 cube sponge was positioned in 8.0 mL of pure water in a 3.5 cm Petri dish. Then, the time for full soaking was measured for each sponge. The measured soaking times were less than 10 s with the exception of the PU III and synthetic rubber sponges, that required more than 60 min for complete saturation; meanwhile, the melamine sponge provided the shortest soaking time of 2.1 s. The PU III and synthetic rubber sponges were excluded from subsequent evaluation due to their poor water uptake.

In the case of the PVA and natural pulp sponges, big internal pores (larger than a few millimeters) are irregularly distributed inside. These randomly distributed large pores increase the uncertainty in the propagation of traversing photons through the sponge and negatively impact the reproducibility of transmission measurements. Therefore, these two sponges were also ruled out from the candidate group. When pore size is considered, the pores in the PU I sponge are too large (3~5 mm approximately), so the generation of photon diffusion enabling of transmission bulk sampling is difficult. Therefore, the PU I sponge was not considered as a potential candidate.

For the remaining PU II, PE I, PE II, and melamine sponges, a solution of the prepared AuNP solution (4.82×10^{10} particles/mL) was individually soaked into each sponge for 1 min and the transmission Raman spectra of these AuNP-incorporated sponges (AuNP sponges) were acquired after drying, as shown in Figure 2. The PU II sponge became exceptionally harder after drying; the transmitting Raman signal crossing the AuNP-incorporated PU II sponge was not observed due to the severe attenuation of the photons by the densified medium. For this reason, the corresponding Raman spectrum is not displayed in the figure. It is desirable that the Raman peaks associated with the sponge are weak and indistinct to allow the easy identification of the spectral features of a target analyte for reliable quantitative analysis. Raman peaks of the AuNP-incorporated PE I and PE II sponges are considerably stronger and more complex compared to those of the AuNP-incorporated melamine sponge. Thus, the melamine sponge, which provides a much lower background Raman signal with less distinct spectral features, is preferred. For reference, pictures of the cubic melamine sponge in a Petri dish before (left) and after (right) soaking with the AuNP solution are shown in the top of Fig. 2.

One last important requisite is that the substrate needs to hold AuNPs firmly without serious leakage during analysis. Based on this,

the melamine sponge is well-suited because it has amino groups and three-nitrogen hybrid rings in its structure that have strong attraction to the AuNP surface, as reported in previous studies.[23,24] Therefore, holding AuNPs within the framework of the melamine sponge is expected to be facile without the need for further chemical modification of the surface. Ultimately, the melamine sponge was selected as the only material for the preparation of TSERS substrates due to its multiple advantages including its fast sample uptake, low background Raman signal, and proper chemical surface for the internal holding of AuNPs. Figure 3 (a) shows an SEM image of the melamine sponge. A sufficient number of pores, which are able to draw the solution inside via capillary action, are apparent, and the pore sizes range from approximately 20 to 100 μm.

Characterization and evaluation of AuNP-incorporated melamine sponge

To initially confirm the incorporation of AuNPs inside the sponge structure, an SEM image of the AuNP-incorporated sponge was acquired, as shown in Fig. 3 (b). AuNPs positioned on the polymer frame are clearly observable. The measured water uptake volume in the 1 cm^3 sponge was 1.11 ± 0.07 mL; therefore, approximately 5.35×10^{10} AuNPs are expected to be housed inside. AuNP sponges were soaked in a 4 μM 4-NBT solution for 10 min and their transmission Raman spectra were collected. Figure 4 displays the transmission Raman spectrum acquired from the 4-NBT-introduced AuNP sponge (designated as 4-NBT-AuNP sponge, blue). The Raman spectra of the 4-NBT-AuNP solution (green) and just the AuNP sponge (red) are also shown for comparison. The spectra are arbitrarily offset for clarity. The spectral features of the 4-NBT-AuNP sponge are distinct and nearly the same as those of the 4-NBT-AuNP solution. This observation again indicates that AuNPs are housed in the sponge. Meanwhile, the Raman peaks of the melamine sponge are nearly unobservable in the spectrum of the 4-NBT-AuNP sponge. The absence of a background Raman signal from the sponge makes it advantageous as a TSERS substrate. The soaking time of 10 min in the 4-NBT solution was determined by varying the soaking time between 1, 5, 10, 20, and 30 min and examining the corresponding intensities of the 4-NBT peaks. The intensities increased up to a soaking time of 10 min, but there was no noticeable increase after this time (data are not shown here).

Since the measurement is based on acquisition of transmitted photons, Raman intensity expects to vary depends on the thickness of sponge. For the investigation, AuNP sponges with thicknesses from 2 to 20 mm (2 mm increments) were prepared and 4-NBT (4 μM) was individually introduced into each AuNP sponge as accomplished above. Then, transmission Raman spectra of these 4-NBT-AuNP sponges were collected. The inset in Fig. 4 shows the variation of peak intensities at 1340 cm^{-1} (the most intense peak, marked by an asterisk) when the thicknesses of AuNP sponges change. The intensities decrease exponential-like with the increase of thickness due to the greater attenuation of Raman photons by scattering as also observed in previous publication.[2] To determine a proper sponge thickness, simultaneous consideration of both sensitivity and ability of bulk sampling for quantitative representation is necessary. The use of thinner thicknesses such as of 2 or 4 mm could be advantageous for acquiring spectra with higher intensity; however, the sampled volumes for spectral acquisition out of the total sponge volume are relatively small and so the bulk sampling ability degrades. When the AuNP sponges are thicker such as over 14 mm, the intensities are too weak, although the sampled volumes substantially increase. Therefore, the 10 mm thickness able to make both needs balanced was chosen for further measurements of samples. When three

transmission Raman spectra collected by illuminating the laser on three different faces (the front, top, and left faces) of a cubic (1×1×1 cm^3) 4-NBT-AuNP sponge were compared, the acquired spectral features are similar to each other (data are not shown here), thereby confirming acceptable quantitative sample representation of the substrate.

To examine the distribution of the AuNPs in the sponge, Raman mapping (based on back-scattering measurements) was performed by covering an area (8.5 × 8.5 mm^2) on one face of the 4-NBT-AuNP sponge. The mapping interval was 150 μm in both the *x* and *y* directions, and a total of 3,364 spectra were collected. Figure 5 shows the resulting Raman mapping image constructed using the intensity of the 1340 cm^{-1} band. The spots of high intensity (red/orange color) are widely distributed over the face, while their distribution is not fully uniform. The high intensity spots are more prevalent around the bottom-right and less common around the top-left. Therefore, the Raman intensities could vary when only a localized portion of the substrate is sampled for spectral acquisition. Therefore, a transmission measurement that enables the laser photons to widely interact with the AuNPs housed in the sponge is a good choice in order to obtain more quantitatively representative SERS spectra.

One important requirement for a reliable TSERS substrate is little or no leakage of the incorporated nanostructures over the course of analysis. As mentioned above, the melamine sponge was selected because it contains amino groups and three-nitrogen hybrid rings that can hold AuNPs within the substrate. These functional groups in the melamine structure can strongly coordinate with the AuNPs via ligand exchange, as reported earlier;[23,24] therefore, compounds containing these functional groups easily aggregate AuNPs, leading to a color change. Thus, colorimetric sensors that rely on this aggregation-induced color change in the presence of melamine have been demonstrated.[23,24] To verify the holding ability of AuNPs inside the sponge, five 4-NBT-AuNP sponges were separately prepared. De-ionized (DI) water was soaked into these sponges and drained out by gently touching them with a water-absorbing tissue. This washing procedure was repeated up to four times and the transmission Raman spectra of these sponges were acquired after each washing step. To get a more representative sampling of the 4-NBT adsorbed on the AuNPs in the sponge, three transmission Raman spectra were collected by illuminating the laser on three different faces of the sponge. Then, the triplicate spectra acquired from each sponge were averaged and the average spectrum was used for evaluation. Figure 6 (a) shows the intensity variation of the 1340 cm^{-1} band with repeated DI water washings of the 4-NBT-AuNP sponges. There is no noticeable intensity variation with the repetition of washings and no significant leakage of internally-housed AuNPs is expected during sample analysis. The substrate-to-substrate reproducibility was estimated by calculating the relative standard deviation (RSD) of the intensities acquired from the five independent 4-NBT-AuNP sponges before DI water washing. The resulting RSD was 10.0 %, which is acceptable for field applications. In addition, the limit of detection (LOD) calculated based on three times of standard deviation of the control measurement was 0.14 nM.

Another important advantage of the TSERS substrate is easy sample enrichment to enhance the sensitivity since the procedure of analyte introduction into a sponge and the depletion of the solvent are easily repeated. To evaluate the ability of sample enrichment, soaking of a 40 nM 4-NBT solution and draining of an aqueous solvent were repeated up to three times using three separately prepared AuNP sponges. The transmission Raman spectra were collected at each enrichment step. Fig. 6 (b) shows the intensity variation of the 1340 cm^{-1} band with up to three repeated sample enrichments. The three time-enrichment makes the intensity doubled (for the 40 nM 4-NBT sample). These results demonstrate the additional analytical advantage of this substrate for sample enrichment when sensitivity

enhancement is required. The sample enrichment can be alternatively realized by simply allowing the AuNP sponge in a sample over a period time. However, the intensity increase started to level off from 10 minutes of soaking as described earlier, so confirming the maximized diffusion of an analyte at this condition. It illustrates that the sample enrichment by natural soaking is slow and able to enrich only a limited amount of analyte. In a meanwhile, the repetition of the suction/drain of a sample makes the enrichment faster and greater.

Measurement of paraquat in various matrices using AuNP sponges

Using the AuNP sponges, the measurement of paraquat (a well-known herbicide) in various matrices (DI water, tap water, river water, and orange juice) was attempted. Initially, seven paraquat samples in DI water (concentration range between 10^{-9} and 10^{-3} M at an interval of 10^{-1} M) were prepared and soaked into the AuNP sponges for measurement. Figure 7 (a) shows the transmission Raman spectra of the AuNP sponges that captured different concentrations of paraquat in DI water. The bottom spectrum (control) was acquired when just DI water was introduced. The intensities of the paraquat peaks elevated with increasing concentration and the most intense band at the 1641 cm^{-1} peak is observable for the 10^{-9} M paraquat sample. Next, different concentrations of paraquat samples (10^{-6}, 10^{-7}, and 10^{-8} M) prepared in both tap and river water were measured as shown in Figs. 7 (b) and (c), respectively. In each case, a spectrum corresponding to the control measurement (the same matrix without the paraquat) is also shown. The overall Raman intensities decrease and the spectral features of both of the control measurements differ from those acquired for the paraquat in DI water. The lowered intensity and dissimilar control spectral features are attributed to the decrease of the available active SERS surface, which is caused by the surface coverage of ionic species in the matrix via charge interaction and adsorption of the contained substances (such as microorganisms) on the surface. Nonetheless, the 1641 cm^{-1} peak is apparent for the 10^{-8} M paraquat samples in both cases.

The measurement of paraquat in orange juice (10^{-3} and 10^{-6} M) was also performed. Fig. 7 (d) shows the transmission Raman spectra of the paraquat-spiked orange juice acquired using the AuNP sponges. The top red spectrum was obtained when the substrate was fully soaked with the 10^{-6} M paraquat sample before being drained. As shown, the fluorescence background that generated from the orange juice dominates and the paraquat peaks are unobservable. However, after depletion of the soaked orange juice, the fluorescence signal disappears and the paraquat peaks can be seen in both samples. This result demonstrates an additional analytical usage of the TSERS substrate for avoiding the matrix fluorescence.

Conclusions

The AuNP-incorporated melamine sponge, which is a TSERS substrate that takes advantage of the useful properties of a sponge (e.g., its fast sample uptake, ability of sample enrichment, and stable polymeric structure), was shown to be simple to prepare and practical for sample analysis. The substrate-to-substrate reproducibility had an acceptable RSD value (10.0 %). The reproducibility is mainly attributed to the transmission spectral acquisition, which allows for bulk interaction of the laser radiation with the internal AuNPs in the sponge. This versatile TSERS substrate also enables easy sample enrichment to enhance sensitivity. A sponge substrate that incorporates more efficient SERS-generating structures (e.g., nanodendrites) is currently under development. In addition, an analytical method utilizing a sponge-based TSERS substrate as a continuous on-line sample enrichment medium for trace analysis is also under way.

Acknowledgment

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012R1A1B3003965). This work was supported by a NRF (National Research Foundation of Korea) Grant funded by the Korean Government (NRF-2011-0008638-Global Ph.D. Fellowship Program).

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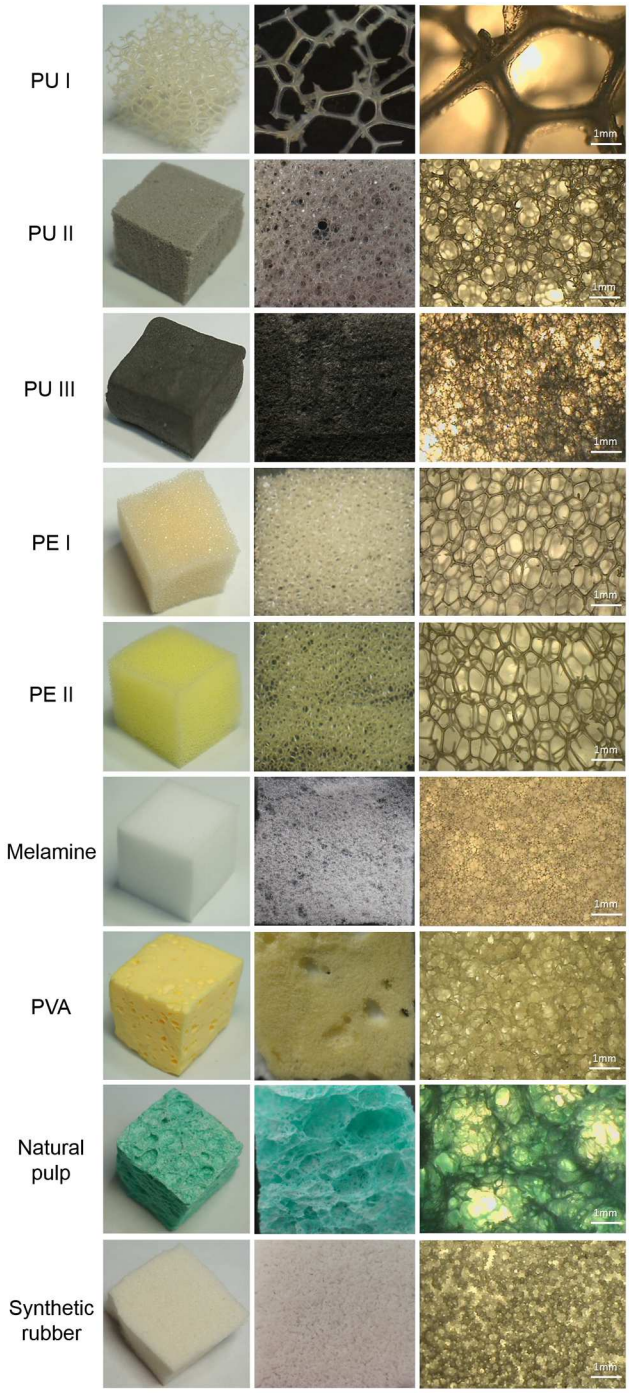


Fig. 1 (a) The images of nine different sponges evaluated for use as a TSERS substrate. The images in the first, second, and third columns show the actual appearances of the sponges (volume: approximately 2.0 - 2.5 cm^3), top-view images (~1.0 × 1.0 cm^2) of thin-sliced sponges, and the corresponding enlarged images with 40-fold magnification, respectively.

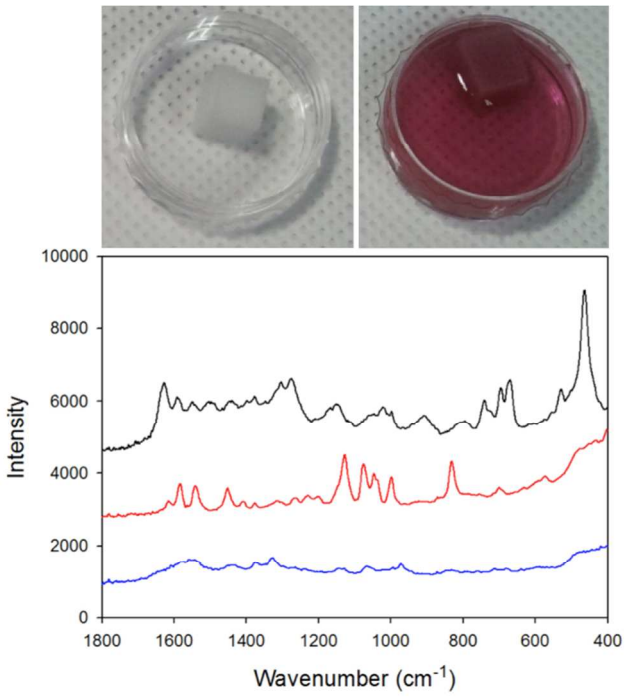


Fig. 2 Transmission Raman spectra of AuNP-incorporated PE I (red), PE II (black), and melamine sponges (blue). The spectra are offset for clarity. Pictures on the top show cubes of the melamine sponge in a Petri dish before (left) and after (right) being soaked with the AuNP solution.

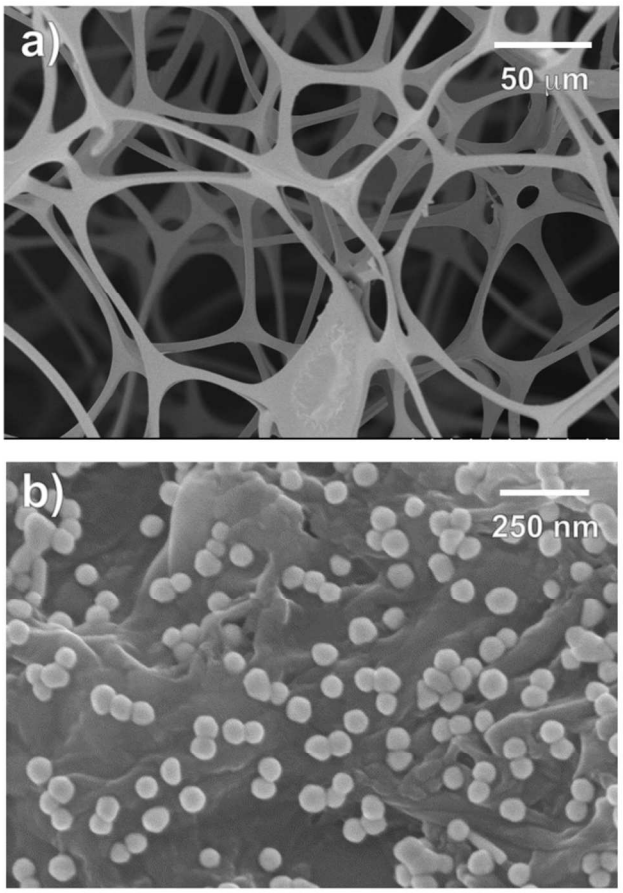


Fig. 3 SEM images of only the melamine sponge (a) and the AuNP-incorporated melamine sponge (b).

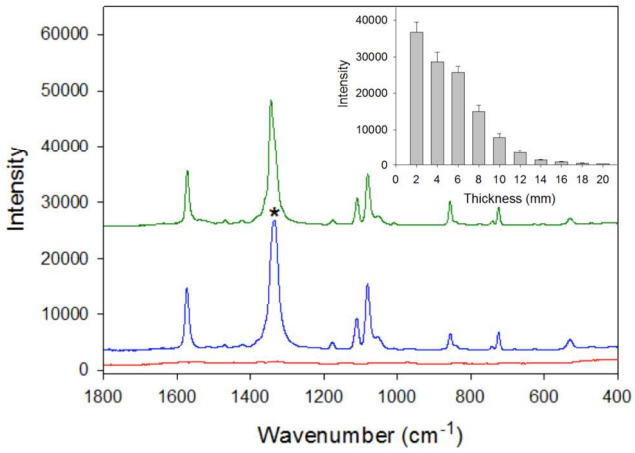


Fig. 4 Raman spectra obtained from 4-NBT-adsorbed AuNP solution (green), 4-NBT-AuNP melamine sponge (blue), and only the AuNP-incorporated melamine sponge (red). The spectra are offset for comparison. The asterisk indicates the most intense 4-NBT peak at 1340 cm^{-1}. The inset shows the variation of Raman intensities of the 1340 cm^{-1} peak when the thicknesses of AuNP sponge vary from 2 to 20 mm (2 mm increments).

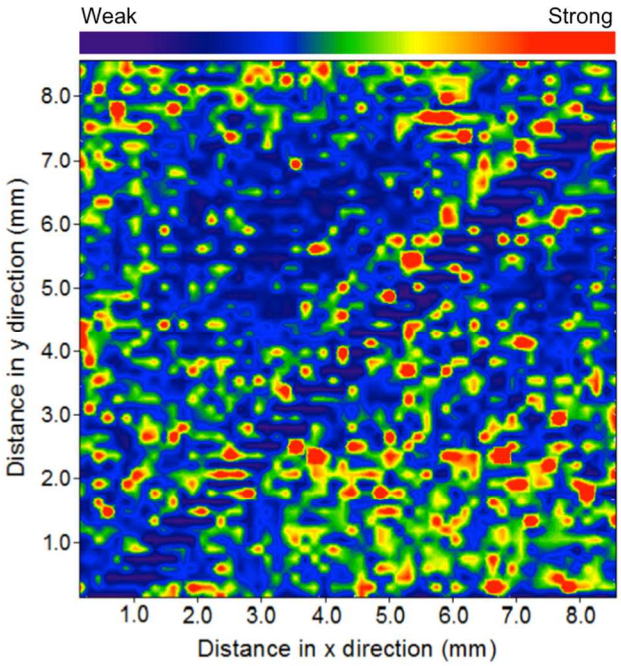


Fig. 5 Raman mapping image on one face of the 4-NBT-AuNP sponge (8.5 × 8.5 mm^2). The image is constructed using the intensity of the 4-NBT band at 1340 cm^{-1}. A total of 3,364 (58 × 58) back-scattering spectra were collected with mapping intervals of 150 μm in both the x and y directions.

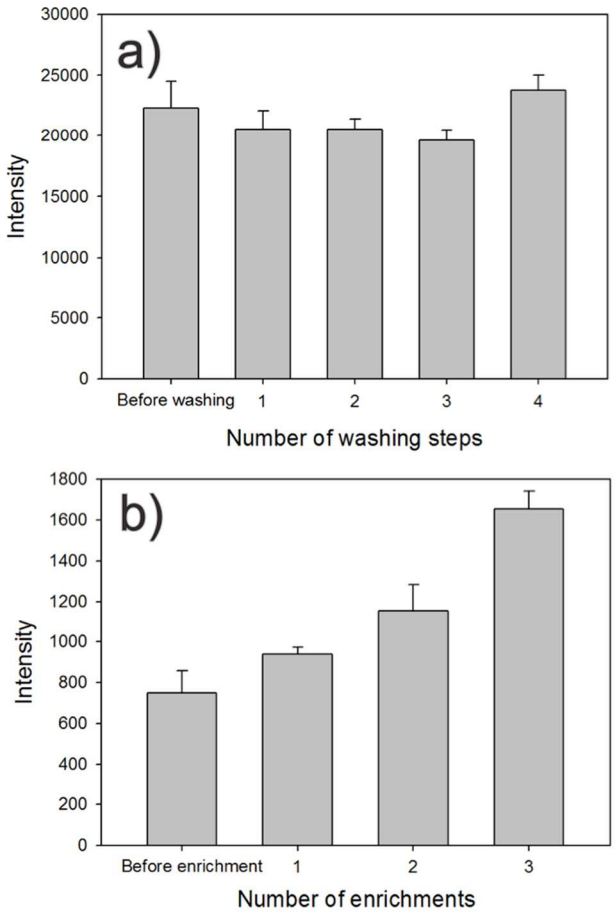


Fig. 6 The intensity variations of the 4-NBT band at 1340 cm^{-1} with repeated DI water washing steps (a) and up to three repeated sample enrichments of 40 nM 4-NBT (b).

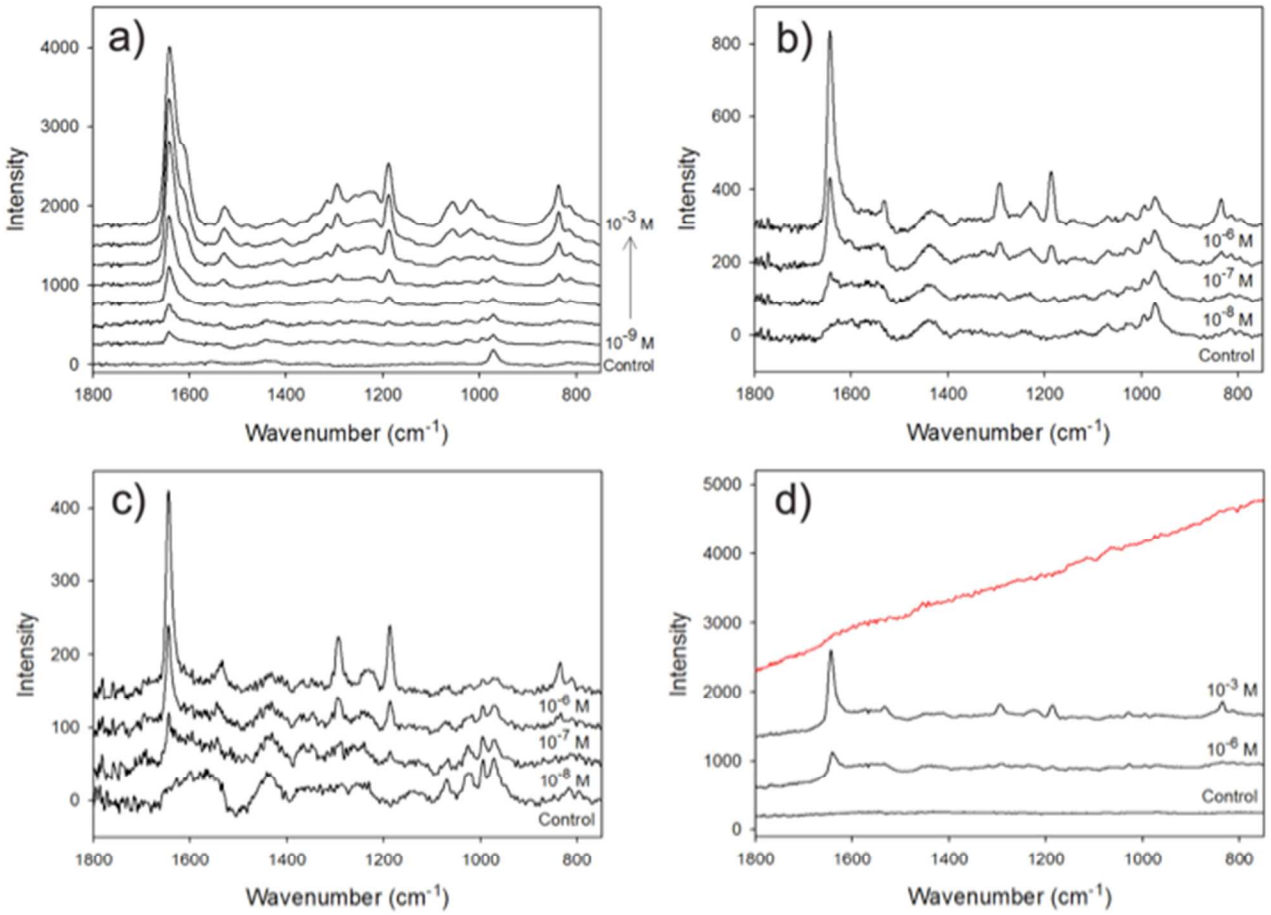
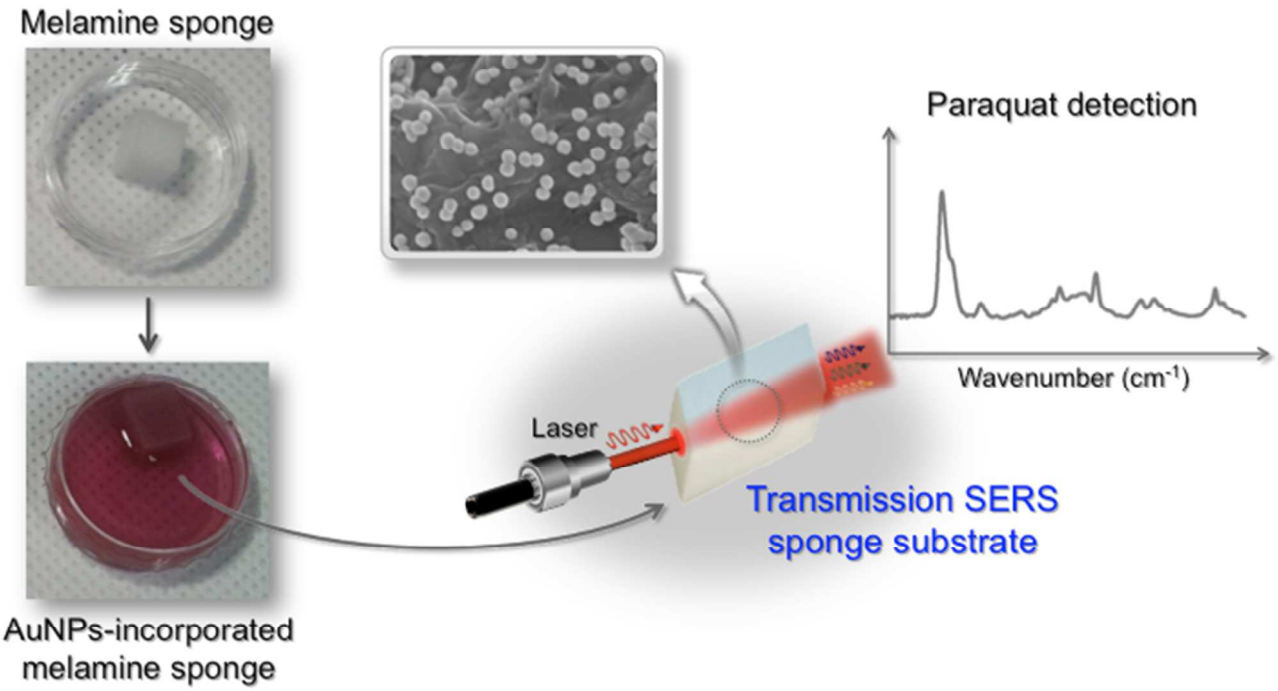


Fig. 7 Transmission Raman spectra of paraquat samples with different concentrations prepared in DI water (a), tap water (b), river water (c), and orange juice (d). The red spectrum was acquired from a AuNP sponge fully saturated with the 10^{-6} M paraquat orange juice sample.



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