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Trichloroethylene sensing in water based on SERS with multifunctional Au/TiO₂ core-shell nanocomposites

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Abstract

Herein we report on a rapid and highly sensitive scheme to detect trichloroethylene (TCE), an environmental contaminant, by surface enhanced Raman scattering (SERS) with multifunctional Au/TiO₂ core-shell nanocomposites as SERS substrates. A facile approach to fabricate TiO₂ shell around gold core nanocomposites is proposed as sensors for TCE detection by SERS. During detection, TCE was first oxidized due to the photocatalytic activity of the TiO₂ shell and the increase in SERS intensity due to the product of TCE photooxidation can be used to determine the concentration of TCE. It should be noted that the SERS of the Raman label, 4-mercaptopyridine (4-MPy) modified onto the gold nanoparticle (GNP) core is in proportion to the product of TCE photooxidation. After optimizing the sample pH, enrichment of the analyte, and the UV exposure time, the methodology developed accomplishes an excellent limit of detection (LOD) (0.038 μ M, ie. ~5 ppb) for TCE in water. Our unique approach based on the synthesized SERS composite to detect TCE, a chlorinated environmental contaminant directly in water could pave the way for the development of a multifunctional nanosensor platform to monitor TCE and the catalytic reactions in a multiplex format.

Introduction

Trichloroethylene (TCE), widely used as a degreasing agent and an intermediate in the production of other chemicals, is a carcinogen and one of the prevalent contaminants of water in the United States of America.^{1–3} There is a strict limit of the TCE in drinking water, e.g. according to the US Environmental Protection Agency (EPA) guidelines, the Maximum Contaminant Level of TCE in drinking water is 5 ppb (0.038 μ M). Until now, the standard method of detection of TCE in water is based on gas chromatography (GC), or GC combined with mass spectrometry.^{4, 5} However, the requirement of GC instrument limits the portability and on-site detection ability. Therefore, there is a strong need to develop a simple, low-cost and sensitive method to monitor TCE for public health purposes. However, only very few techniques can transfer the presence of TCE to a detectable signal. Among biosensor approaches, bacterial biosensors^{6, 7} have been shown to detect TCE but has limited utility because of the lifetime of the biosensors. Besides the bacterial biosensor-based approaches, TiO₂ has also been used for the cleanup of TCE due to its photocatalytic activity.^{8, 9} Gas sensors based on TiO₂ have also been developed to detect TCE by

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determining the product of its photocatalytic oxidization.^{10, 11} However, an approach to detect TCE with TiO₂ in liquid samples is rarely reported, possibly due to the complexity of the synthesis of TiO₂-based nanomaterials and the lack of analytical technique to characterize TiO₂ catalyzed TCE photooxidation. Methods to sensitively detect chlorinated compounds in water will significantly benefit the environmental community in routine monitoring and remediation.

In the past decade, it has been reported that nanomaterials based on TiO₂ address various applications related to environment clean up and in solar energy due to its physical and chemical stability, nontoxicity and highly porous structure, especially its high photocatalytic activity.^{12–14} Past work by several have shown that the integration of TiO₂ and Au could yield a remarkable improvement in the photocatalytic activity because Au can decrease the band gap energy of TiO₂.^{15, 16} Until now, most of the Au/TiO₂ composites are based on TiO₂ supported Au nanoparticles (GNPs), such as TiO₂ films loaded with GNPs and TiO₂ nanoparticles loaded with GNPs.^{17–19} Meanwhile, recent research has shown that TiO₂ wrapped GNPs exhibited tunable photoreactivity.²⁰ Therefore, it is reasonable to expect that Au/TiO₂ core-shell nanostructures can extend the applications based on the improved photocatalytic property of TiO₂. Numerous strategies for the synthesis of TiO₂ supported GNPs have been reported, however methods for the synthesis of Au/TiO₂ core-shell structures are limited. The common hydrothermal synthesis route based on TiF₄ is time-consuming,^{20, 21} while the nanostructures prepared with microwave contain a thick TiO₂ shell.²² Thus fast, reliable, and facile route to synthesize Au/TiO₂ core-shell nanostructures will have a broad interest in addition to demonstrating the utility of the nanocomposite sensors for contaminant monitoring.

We propose a simple synthesis protocol for the preparation of Au/TiO₂ core-shell structures and to demonstrate its application for the detection of TCE in a liquid format. Compared to the past hydrothermal routes, in our approach, the TiO₂ shell was prepared in a rapid manner. The GNPs as cores modified with Raman tags, 4-mercaptopyridine (4-MPy) before the TiO₂ shell structure preparation provided a strong SERS activity. It is well known that SERS can greatly enhance the Raman signal from Raman tags,^{23, 24} thus it is possible to improve the sensitivity of SERS-based analytical method to monitor chemical contaminants in water.²⁵ It is known that the SERS spectra of 4-MPy is sensitive to pH.^{26, 27} Past reports have demonstrated that based on the photocatalytic activity of TiO₂, TCE would be oxidized to generate HCl to result in an increase in the pH in the TiO₂ shell.^{10, 28} Thus, by monitoring the change in SERS intensity of 4-MPy it is possible to report on the extent of photocatalytic oxidation of TCE in the TiO₂ shell which can be used as an indicator of TCE in water. Integrating the photocatalytic activity of the TiO₂ shell, the SERS enhancement of the GNP core and the pH-response of 4-MPy, the Au/TiO₂ core-shell multifunctional nanocomposites presents a simple design for an environmental sensor.

Experimental section

Materials

Sodium citrate, HAuCl₄, 4-MPy, phenol, titanium-(triethanolaminate) isopropoxide (N((CH₂)₂O)₃TiOCH(CH₃)₂, TTEAIP) and TCE were purchased from Aldrich.

Isopropanol, chloroform and toluene were obtained from Macron Fine Chemicals. All reagents were used as received.

Synthesis of Au@TiO₂ core-shell multifunctional nanostructures

All glasswares used in the described experiments were washed in a bath of fresh 3:1 HCl:HNO₃ (aqua regia) solution and rinsed with water purified by milli-Q system. GNPs used as core were synthesized based on the reported method.²⁹ Typically, 1 ml of 1 wt% HAuCl₄ was added to 100 ml of water and heated to boiling. Then 1 ml of 1% sodium citrate was added to the boiling solution under strong stirring. The obtained solution was kept at a boiling state for 10 minutes and cooled in room temperature and stored at 4°C. To modify GNPs with Raman tag, 8 ml of the as-prepared GNPs were centrifuged and redispersed in 4 ml H₂O, followed by the addition of 240 µl of 10⁻⁵ M 4-MPy and kept overnight. The modified GNPs were centrifuged again to remove the unreacted 4-MPy and redispersed in 2 ml of H₂O.

Multifunctional Au/TiO₂ core-shell nanostructures were prepared based on the hydrolysis of TTEAIP in isopropanol. The procedure was developed based on prior work³⁰ and optimized to accommodate the functionalized GNPs. Briefly, 4.34 µl of 8 wt% of TTEAIP is added to 28 ml of isopropanol, and then injected with 2 ml of 4-MPy modified GNPs. The obtained solution was stirred for 30 minutes at room temperature and then heated to boiling and refluxed for 30 minutes with continued stirring. After cooling to room temperature, the product was centrifuged and washed with ethanol three times and then with H₂O three times respectively. The washed product was then redispersed in 3 ml H₂O.

Detection of TCE

18 µl of Au/TiO₂ core-shell nanostructures was mixed with 2 ml of TCE in serial concentrations, then 2 µl of 1 mM H₂O₂ was added. The obtained samples were kept in the dark for 30 minutes and then exposed to UV light (Rad Free UV lamp 365 nm, Schleicher & Schuell) for 1 hour. SERS spectra of the samples were then recorded and analyzed.

Characterization

Transmission electron microscopy (TEM) images and energy-dispersive X-ray (EDX) spectra of the samples were recorded with a FEI Tecnai G2 20 equipped with an energy-dispersive X-ray detector in operation at 100µkV. UV-vis spectra of the Au/TiO₂ core-shell structures were collected with a Jasco V570 UV/Visible/NIR spectrophotometer (Jasco, Inc., Easton, MD). SERS spectra were obtained with a SENTERRA confocal Raman system (Bruker Optics, Billerica, MA) with a 20× long WD objective and irradiated with 785 nm laser (100 mW, 5 seconds integration time). To measure the intensity of the SERS peaks, the background signal from the glass container shown in Fig. S1 is subtracted from all of the obtained spectra. No further post-processing step is applied to the SERS spectra.

Results and discussion

The fabrication of multifunctional Au/TiO₂ core-shell nanocomposites and TCE detection concept using multifunctional nanostructures are shown in Scheme 1. In our work, the GNP

cores were used as SERS substrates with strong SERS activity and 4-MPy was used to represent the formation of the TCE oxidation product, HCl, which induces a pH dependent response from 4-MPy, for sensitive detection of TCE in water. It should be noted that the 4-MPy modification will affect the stability of GNPs, thus, during the TiO₂ shell fabrication, low aggregates of GNPs may form. After 4-MPy modification, a TiO₂ shell was formed around the GNP core due to the hydrolysis of TTEAIP. As a first step in detection, the washed nanocomposites were mixed with the sample containing TCE. It has been reported that TiO₂ could adsorb TCE molecules.¹⁰ In our work, this adsorption process could serve as an enrichment step to increase TCE concentration in the TiO₂ shell to further improve the LOD. The mixture was then exposed to UV light. Under UV light, TCE is oxidized due to the photocatalytic activity of TiO₂ to generate oxidation products including HCl.^{10, 28} Production of HCl induces a change in the pH of the TiO₂ shell which will influence the SERS spectra of 4-MPy in proportion to the concentration of TCE in the sample. As shown in Fig. S2, the SERS intensity of the GNPs modified with 4-MPy as the cores of the nanocomposites increase with higher concentration of hydrions, suggest that during our detection, the HCl generated by the photocatalytic oxidization of TCE in the TiO₂ shell will improve the SERS intensity which could be used as indicator of the TCE concentration. Benefiting from the enrichment of TCE due to TiO₂ shell and SERS enhancement of the GNP core, an excellent LOD could be achieved.

Based on the hydrolysis of TTEAIP, TiO₂ shell was formed around the 4-MPy modified GNP or aggregates of two or three GNPs. To characterize the obtained nanostructures, TEM images of the products are shown in Fig 1. It can be seen in Fig 1A that when 4.34 μ l of 8% wt TTEAIP isopropanol solution was added, a very thin TiO₂ shell was obtained, for a thickness of less than 5 nm, and the surface of the TiO₂ shell was smooth. Fig 1B shows the morphology of the obtained Au/TiO₂ core-shell nanostructures. It can be noted that in some particles the TiO₂ shell wraps a single GNP while in some others the TiO₂ shell encapsulates aggregates of two or three GNPs. The aggregation of GNPs can be attributed to the reduced stability of GNPs due to the modification of 4-MPy.

The UV-vis spectra of the obtained Au/TiO₂ core-shell nanostructures is shown in Fig 2A. As a reference, the UV-vis spectra of GNPs were also recorded. It is known that TiO₂ yields an absorption peak in the UV region.^{31, 32} Compared with the UV-vis spectrum of GNPs the obtained nanostructure showed a higher absorption in the UV region, suggesting the formation of TiO₂ shell. It is known that 40 nm GNPs have a peak at $\sim$ 528 nm,³³ the red shift of the peak in the spectrum of the Au/TiO₂ core-shell nanostructure as well as the increase in UV-vis absorption in the long wavelength region can be attributed to the slight aggregation of the GNP cores. The EDX spectrum in Fig 2B used to characterize the nanocomposites also indicates the presence of Au and Ti in the Au/TiO₂ core-shell nanocomposites.

In the proposed detection procedure the TCE concentration is determined according to the change in the SERS intensity of the Au/TiO₂ core-shell nanostructures, and the SERS activity of these sensors is critical to the detection performance. As shown in Fig 2C the SERS spectrum recorded for these nanocomposites shows distinct peaks of 4-MPy. Three peaks located at 1012, 1055 and 1095 cm⁻¹ were observed, which are attributed to the 4-

MPy fingerprint on the modified GNP cores.^{26, 34} For the purpose of TCE detection, an intense SERS intensity will lead to better detection sensitivity, therefore we chose the intensity of the peak located at 1095 cm^{-1} for optimization of the detection condition and determination of TCE concentration.

As described above, there is a change in pH induced by the production of HCl due to the photocatalytic oxidation of TCE, and the change in pH will trigger the SERS intensity change in the enhanced spectra of 4-MPy. Therefore to assess the change in the 4-MPy spectra with respect to pH in the Au/TiO₂ core-shell nanosensors, the nanocomposites were evaluated in a serial pH and the SERS intensity of the peak at 1095 cm^{-1} of the 4-MPy spectra are shown in Fig 3A. To amplify the pH change resulting from HCl production, the pH of the samples was adjusted to be alkaline. It was observed that the SERS intensity decreased when the pH increased from 7 to 11. Meanwhile, for detection, the generated HCl due to the photooxidation of TCE could reduce the pH in the TiO₂ shell. Therefore it was believed that the pH change due to the photooxidation of TCE could contribute to an increase in the SERS intensity, which was utilized to determine the TCE concentration in the samples. To estimate the effect of pH of the samples, the SERS intensity change due to $1\text{ }\mu\text{M}$ TCE was assessed and R was evaluated to assess the change, which was defined as, $R = (I - I_0)/I_0$. Here, I is the intensity of the peak at 1095 cm^{-1} of the samples with $1\text{ }\mu\text{M}$ TCE and I_0 is the intensity of the peak at 1095 cm^{-1} of the blank. It can be seen that greater the value of R better is the sensitivity. The R obtained in serial pH was shown in Fig 3B. The largest R was obtained when the pH of the solution was 9. Therefore the pH of the samples was adjusted to be 9 to achieve the best detection sensitivity.

It was established that for TCE photooxidation, energy from the photons due to UV exposure is necessary; while to assist oxidation, additive oxidant is also needed.¹⁰ To further show that the increase in SERS intensity of the nanocomposite sensors was induced by TCE photooxidation, two negative control samples with $1\text{ }\mu\text{M}$ TCE were tested. In one of the samples, the oxidant H₂O₂ was absent and in the other there was no exposure to UV light. It can be noted that in Fig 3C without the added H₂O₂, the R of the control was negative, indicating that without TCE oxidation the spectra of the nanocomposite sensors will not increase. For the samples not exposed to UV light, R was even less than that of the samples without the added H₂O₂. Results from the two negative controls show that TCE could reduce the SERS intensity of the sensors without oxidation. It should be noted that the R values for the two negative controls are different. A possible reason could be that for the samples without the added H₂O₂ the amount of oxidant in the samples such as the dissolved oxygen was not sufficient to complete the oxidation of TCE. Therefore with UV exposure some TCE molecules in the samples without the added H₂O₂ were oxidized, resulting in a slight increase in SERS intensity. However, for the samples without UV exposure, TCE oxidation did not occur and thus the R value was low. The change in the SERS signal from the samples without the added H₂O₂ or without UV exposure further provided proof that TCE oxidation based on the photocatalytic activity of TiO₂ shell is a key factor influencing the intensity of the SERS peak.

The enrichment time of the nanocomposite sensors for TCE molecules and the UV exposure time were optimized to achieve the best detection results. The change in the SERS spectra of

the samples for different enrichment and UV exposure time are shown in Fig 4. From Fig 4A, it can be seen that the R values of the samples reduced when the enrichment time is longer than 30 minutes, suggesting that the adsorption of TCE to the TiO_2 shell was fast. Similarly, a decrease in the R value can be noted for higher concentration of TCE. As shown in Fig. S3, it can be seen that the R values of the samples with 10^{-4} M TCE also reduces for enrichment times longer than 30 minutes. Considering the low boiling point (87.2°C) and high vapor pressure (58 mm Hg at 20°C) of TCE, the reduction in the value of R could possibly be attributed to volatilization of TCE. Fig 4B shows the change in the SERS spectra for varying UV exposure times after a 30 minute enrichment time. Experiments show that the biggest change in R was noted for a UV exposure time of 60 minutes. The increase in R values from 0 to 60 minutes of UV exposure can be attributed to the formation of increased TCE oxidation products due to longer UV exposure, while the decrease of R value after 60 minutes can be assigned to the diffusion of TCE photooxidation products in the TiO_2 shell. After 60 minutes the concentration of the unreacted TCE reduced in the shell and the diffusion of oxidation products was faster than the photooxidation, resulting in a lower concentration of oxidation products in the TiO_2 shell and consequently a reduction in the SERS signal. Based on the results of the optimization, 30 minutes of enrichment time and 60 minutes of UV exposure time was chosen.

To demonstrate the SERS intensity of the nanocomposite sensors' response to varying levels of TCE, the SERS spectra and SERS intensity of the peak at 1095 cm^{-1} versus the concentration of TCE is shown in Fig 5. As shown in Fig 5A, an increase in the SERS intensity was observed for higher concentration of TCE. Per the calibration curve plotted in Fig 5B it can be observed that the SERS intensity of the nanocomposite sensors increased with respect to the concentration of TCE. A linear SERS response was established from $0.1\text{ }\mu\text{M}$ to 0.1 mM ($R^2=0.993$) with a limit of detection as low as $0.038\text{ }\mu\text{M}$ (5 ppb), which is lower than the reported methods developed for TCE detection in water and available for the EPA's Maximum Contaminant Level.⁶ TEM images show that the aggregation and morphology of the GNP cores are not very uniform, which is a possible reason for the deviation in the intensity of the Raman peaks. Meanwhile we investigated the SERS response of two other peaks at 1013 and 1055 cm^{-1} to TCE concentration. As shown in Fig. S4 and Table S1, the comparison indicates that based on the SERS intensity of peak at 1095 cm^{-1} the lowest LOD is achieved because of the higher enhancement. The proposed approach reports one of the lowest LOD compared to the biosensor approaches for TCE detection in water with a potential for detecting other analytes. With water samples from the local river

To demonstrate the selectivity of the proposed detection method, chloroform, phenol and toluene, some of the other general environmental pollutants, were tested as negative controls. As shown in Fig 6, compared with the blank, only the samples with TCE exhibited an increased SERS intensity, while the intensity of 4-MPy did not increase in the samples with $1\text{ }\mu\text{M}$ of the other pollutants. To estimate the influence of chloroform oxidization using our detection strategy, we tested samples with higher concentrations of chloroform. As shown in Fig. S6, it can be noted that the SERS intensity from samples with 10^{-2} M chloroform is even weaker than that from 10^{-6} M TCE, indicating a very minor influence of chloroform to our detection.

Conclusion

Multifunctional Au/TiO₂ core-shell nanocomposites were fabricated to detect TCE in water by SERS. The facile synthesis of TiO₂ shell around GNPs reported in this work is simpler than the existing hydrothermal-based synthesis approaches. Benefiting from the enrichment of the TiO₂ shell and the SERS enhancement of the GNP core, excellent detection sensitivity was achieved. After optimization of the sample pH, the enrichment time and duration of UV exposure, the LOD of the proposed method was established to be 0.038 μ M (5 ppb), the lowest reported using the biosensor approaches for monitoring TCE in water. By integrating SERS enhancement and the photo-catalysis feature, our method presents a unique route to the detection of TCE contamination in water and lays the groundwork for environment monitoring.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig 1.
TEM images of Au/TiO₂ core-shell nanocomposites synthesized with 4.34 μ l of 8% wt TTEAIP isopropanol solution.

Fig 2.
UV-vis (A), EDX (B) and SERS (C) spectra of Au/TiO₂ core-shell nanocomposites.

Fig 3.

SERS intensity of the peak at 1095 cm^{-1} [mean $\pm$ SD, $n = 3$] (A) of the Au/TiO₂ core-shell nanocomposite sensors and R values [mean $\pm$ SD, $n = 3$] at $1\text{ }\mu\text{M}$ of TCE (B) in different pH. Plot of R [mean $\pm$ SD, $n = 3$] at $1\text{ }\mu\text{M}$ of TCE in the samples without H₂O₂ or UV exposure and with H₂O₂ and UV exposure (C). The enrichment time of the samples shown in B and C was 30 minutes and the UV exposure time was 60 minutes.

Fig 4.

SERS intensity changes [mean $\pm$ SD, n = 3] in the samples at different duration of enrichment (A) and UV exposure (B).

Fig 5. SERS spectra with serial concentration of TCE (average of the SERS spectra without background subtraction) (A) and calibration plot in response to TCE concentration based on the intensity of the peak at 1095 cm^{-1} [mean $\pm$ SD, $n = 5$] (B).

Fig 6.
SERS intensity of the peak at 1095 cm^{-1} [mean $\pm$ SD, $n = 3$] from blank and the samples with $1\text{ }\mu\text{M}$ of TCE, chloroform, phenol and toluene.

Scheme 1.

Schematic of the synthesis concept of multifunctional Au/TiO₂ core-shell nanocomposites and detection of TCE in water.