Multifunctional satellite $\text{Fe}_3\text{O}_4\text{-Au@TiO}_2$ nano-structure for SERS detection and photo-reduction of Cr(VI)

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HIGHLIGHTS

- A core-satellite structured $\text{Fe}_3\text{O}_4\text{-Au@TiO}_2$ substrate was prepared.
- The substrate can be used to monitor Cr(VI) with evident sensitivity lasting 30 days.
- The Cr(VI) photo-reduction can be in situ monitored by SERS.
- This platform provides an alternative method for quantitative determination of Cr(VI) .

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:

Received 1 September 2016

Received in revised form 9 October 2016

Accepted 27 October 2016

Available online 28 October 2016

Keywords:

SERS

$\text{Fe}_3\text{O}_4\text{-Au@TiO}_2$

Core-satellite

Photo-reduction

Cr(VI)

ABSTRACT

Exposure to hexavalent chromium [Cr(VI)] poses a serious health threat. Thus, accurate field analysis and efficient Cr(VI) reduction are of great importance. The motivation of this research was to synthesize a multifunctional satellite $\text{Fe}_3\text{O}_4\text{-Au@TiO}_2$ nano-structure for surface enhanced Raman scattering (SERS) detection and photo-reduction of Cr(VI) . Our experimental results and three-dimensional finite difference time domain (FDTD) simulation suggest that coating $\text{Fe}_3\text{O}_4\text{-Au}$ with a TiO_2 layer 2–6 nm thick can protect SERS substrates from direct contact and reaction with Cr(VI) , as well as enrich Cr(VI) in close proximity to Au NPs to facilitate its SERS detection. The SERS response exhibited a concentration dependence up to $5\ \mu\text{M}$ with a detection limit of $0.05\ \mu\text{M}$. The SERS substrate exhibited an excellent selectivity for Cr(VI) over other coexisting ions and resulted in a satisfactory quantitation in complicated environmental matrices. In addition, the Cr(VI) reduction photo-catalyzed using this multifunctional material followed the first-order kinetics and the reduction process was monitored in situ with the SERS effect, and yielded a decrease of almost 80%. This novel platform provides an alternative method for the quantitative determination and remediation of Cr(VI) .

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1. Introduction

Chromium (Cr) exposure threatens human health [1]. The toxicity and mobility of chromium depend on its chemical valence, where aqueous Cr(VI) is more toxic than Cr(III) [2]. Thus, accurate field analysis and efficient reduction of Cr(VI) are of great impor-

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tance [2,3]. Though it remains a challenge, it is even more desirable for these two aims to be achieved on a single platform. Our motivation, therefore, was to set up such a multifunctional platform that would integrate effective Cr(VI) adsorption, ultrasensitive detection, and superior Cr(V) reduction activity.

We propose that such a desire can be fulfilled using a single core-satellite material, $\text{Fe}_3\text{O}_4\text{-Au@TiO}_2$ (FAT). This nanocomposite magnetic material can actively concentrate Cr(VI) and be rapidly separated from water, and subsequently quantify Cr(VI) using a surface enhanced Raman scattering (SERS) effect. The use of SERS in environmental analysis is becoming more popular due to its high sensitivity [4–6], rapid response [7], and molecular structural fingerprint [8–10]. Cr(VI) analysis using SERS has been reported on Au nanoparticle (NP) substrates with a detection limit ranging 0.6–48.1 μM [11–13]. Recently, we fabricated $\text{Fe}_3\text{O}_4\text{@Ag}$ SERS substrates and improved the Cr(VI) detection limit of SERS by lowering it to 0.1 μM [14]. This sensitivity improvement may be a result of immobilized hot spots on the core-satellite structure [15–19].

We hypothesize that coating $\text{Fe}_3\text{O}_4\text{@Au}$ with a nm-thick layer of TiO_2 would provide multiple benefits. First, by protecting SERS substrates from directly contacting and thus reacting with an analyte, it would extend the lifetime of the substrate. Second, it would enrich analytes in close proximity to Au NPs, which would facilitate SERS detection. Such a concept has been proven successful using shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) to detect pesticides on fruit [20]. TiO_2 was chosen because it is reported to be SERS-active due to charge transfer between adsorbed molecules and TiO_2 NPs [21]. In addition, it is the most commonly used photo-catalyst and has successful application in Cr(VI) photo-reduction, mainly due to its chemical stability and high catalytical activity [22–26].

The objective of this study was to fabricate FAT SERS substrates to take advantage of multiple phenomena: the magnetic separation of Fe_3O_4 , SERS performance of Au NPs, and highly efficient photo-reduction activity of ultrathin TiO_2 film. Our experimental results and three-dimensional finitedifference time domain (FDTD) simulation suggest that decoration with a 2–6 nm layer of TiO_2 can not only exhibit electromagnetic enhancement of Cr(VI), but also photo-catalytically reduce and remediate Cr(VI). This novel platform provides an alternative method for the quantitative determination and degradation of Cr(VI).

2. Experimental

2.1. Chemicals and materials

Ferric chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$), sodium acetate (NaAc), tetrabutyl titanate, isopropyl alcohol, nitric acid (HNO_3), potassium chromate (K_2CrO_4), $\text{HAuCl}_4\cdot 4\text{H}_2\text{O}$, sodium chloride (NaCl), chromium chloride (CrCl_3) and trisodium citrate dehydrate were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Tetraethyl orthosilicate (TEOS), poly-(diallyldimethylammonium chloride), (PDAA, Mw = 200000–350000, 20% in H_2O) and poly(styrenesulfonate) (PSS, Mw = ~70000, 30% in H_2O) were purchased from Aldrich Scientific Ltd. (USA). Aqueous ammonia solution, absolute ethanol, ethylene glycol (EG) (>99.7%), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3$), sodium m-arsenite (NaAsO_2), trisodium arsenate ($\text{Na}_3\text{AsO}_4\cdot \text{H}_2\text{O}$), calcium oxide (CaO), cadmium chloride (CdCl_2), copper chloride (CuCl_2), mercuric chloride (HgCl_2), potassium chloride (KCl), magnesium chloride hexahydrate ($\text{MgCl}_2\cdot 6\text{H}_2\text{O}$), sodium chloride (NaCl), lead nitrate ($\text{Pb}(\text{NO}_3)_2$), potassium antimony tartrate hemihydrate ($\text{KSbC}_4\text{H}_4\text{O}_7\cdot 1/2\text{H}_2\text{O}$), zinc chloride (ZnCl_2), and potassium pyroantimonate ($\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7\cdot 4\text{H}_2\text{O}$) were purchased from Beijing Chemical Reagents Company (China).

Milli-Q water (>18.2 M Ω) was used in all experiments. All reagents were of analytical grade and were used without further purification. The stock solution of HAuCl_4 (2 wt% in water) was prepared by dissolving $\text{HAuCl}_4\cdot 4\text{H}_2\text{O}$ in water.

2.2. Synthesis of satellite structured FAT

The $\text{Fe}_3\text{O}_4\text{@SiO}_2\text{-Au}$ (FA) NPs were synthesized following a previously reported method [15]. The colloid TiO_2 NPs were synthesized using modified versions of previous methods [27,28]. Briefly, a solution of 12.5 mL of tetrabutyl titanate (98%) was added to 4 mL of isopropyl alcohol. The mixture was shaken until a homogeneous solution appeared. Then, the mixture was added dropwise to a solution containing 150 mL of DI water and 2 mL of HNO_3 , with vigorous stirring and at 70–80 °C until transparent colloids were obtained. To coat the FA with TiO_2 , polyelectrolyte functioned FA-PSS (–) was prepared through the layer-by-layer (LBL) method [15]. Then, 3 mL FA-PSS (–) (10 mg/mL) was dispersed in 1–20 mL transparent TiO_2 colloids and shaken for 20 min (27 °C, 170 r min^{–1}). The final FAT substrates were collected using a magnet, then washed with DI water six times.

2.3. Sample preparation

For SERS analysis, different samples containing Al^{3+} , As(III), As(V), Ca^{2+} , Cd^{2+} , Cu^{2+} , Hg^{2+} , K^+ , Mg^{2+} , Na^+ , Pb^{2+} , Sb(III), Sb(V), Zn^{2+} , Cr(III) and Cr(VI) were prepared by diluting each stock solution separately in DI water. The FAT substrate (0.3 mg) was immersed in a 1 mL Cr(VI)-containing solution. Then, the products were assembled by applying a magnetic field and exposed to a laser to measure the SERS signal with signal integration time = 1 s.

To validate SERS analysis, environmental samples, including chromite ore processing residue (COPR) and Cr(VI)-containing industrial wastewater, were also analyzed with ICP-OES. COPR weighing 1 g was dispersed in 10 mL of DI and shaken for 24 h. Then COPR and wastewater were filtered to form a Cr(VI) stock solution.

2.4. Photocatalytic activity test

FAT NPs massing 0.6 mg and 2 mL of a 100 μM Cr(VI) aqueous solution were put in a small square glass tank. A UV lamp (254 nm, 500W) was used as the light source, and was located 5 cm away from the glass tank. The start time was calculated once the light was turned on. At various irradiation times, 120 μL of a mixed solution was extracted. The products were collected with the help of a magnet, then exposed to the laser to measure the SERS signal.

2.5. Apparatus

The UV-vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The morphology and EDS of the NPs were characterized using high-resolution transmission electron microscopy (HR-TEM, JEM-2010, JEOL) and field emission scanning electron microscopy (FESEM, SU-8020, Hitachi). Raman spectra were obtained using a portable Raman spectrometer (Enwave Optronics, Inc. USA) with a 4 cm^{–1} resolution and 100 μm beam size at the excitation energy of 785 nm. X-ray powder diffraction (XRD) data were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA using a Cu-target tube and a graphite monochromator. Scans were made in the 2 θ range of 10°–90° with a step size of 0.01° and a count time of 2 s per step. ICP-OES data were obtained using Inductively Coupled Plasma Optical Emission Spectrometry 8000.

FDTD simulation: The distribution of electromagnetic field intensity around the FA and FAT nanostructures was calculated using the FDTD method. The mesh size was 1 nm. The calculation time

Fig. 1. (A) Schematic illustration of the fabrication process of the FAT core-satellite structure. SEM image of Fe_3O_4 (B) and FA satellite structured nano-composite (C). (D) Zeta-potentials during the fabrication process of the FAT. TEM image of FAT for low magnification (E) and high magnification (F), the scale bars represent 200 nm and 50 nm, respectively. (G) Typical XRD patterns of FA (red line) and FAT (black line). EDX mapping of Fe (H), Au (I), Ti (J) and the corresponding EDX spectra (K). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

was 1000 fs. For the FA model, a 374 nm Fe_3O_4 @ SiO_2 core was surrounded by satellite Au NPs (20 nm) with a 5 nm gap between Au NPs. For the FAT model, a 2 nm layer of TiO_2 coated the FA. The distance between the core and its satellites was set to 0 nm.

3. Results and discussion

3.1. Synthesis and characterization of FAT

The FAT core-satellite structure with uniform distribution was prepared through an LBL assembly process, as schematically illustrated in Fig. 1A. The Au NPs (20 nm) were uniformly distributed on Fe_3O_4 @ SiO_2 (Fig. 1B) beads to form the core-satellite FA hetero-nanostructure (Fig. 1C). Positively charged TiO_2 (+43 mV) then

coated the surface of negatively charged FA (−25 mV) due to electrostatic interactions to form a positive charged FAT (+22 mV, Fig. 1D).

The morphology and structure of FAT were characterized using TEM (Fig. 1E–F). The TiO_2 layer was immobilized on the surface of FA. To further confirm the formation of FAT, EDX elemental mapping was carried out to identify the elemental distribution status. From the EDX elemental mapping (Fig. 1H–K), it can be observed that the signal points in green, blue, and red correspond to Fe, Au, and Ti, respectively, which confirm the presence of Ti. These results further indicate that the FAT nanoparticles were successfully synthesized and a 2–6 nm TiO_2 layer homogeneously coated the FA (Fig. 1F, Fig. S1). The XRD patterns of FA (red line) and FAT (black line) are displayed in Fig. 1G. The peaks observed at the 2θ values of 30° , 35.3° , 57.0° , and 62.4° represent the [220], [331], [511], and [440] planes of the cubic phase of Fe_3O_4 , respectively [29]; while

Fig. 2. Raman spectra of Cr(VI) with concentrations ranging from 0.01 μM to 5 μM on (A) FA and (B) FAT nanocomposites, signal collection time was 1 s. (C) Calibration curve for Cr(VI) from 0.05 to 5 μM on FAT and FA. The calibration uses the most intensive SERS band at 788 cm^{-1} . The FDTD model predicted electric field distributions for FA (D) and FAT (E) with a 785 nm excitation. (F) The simulated SERS EFs, as estimated from $E_{\text{loc,max}}/E_0^4$ for FA and FAT.

the peaks at 2θ values of 38.2° , 44.6° , 65.0° , and 78.3° correspond to the [111], [200], [220], and [311] planes of Au [29]. No diffraction peaks referring to TiO_2 were observed on the FAT, which indicates that the outermost layer of TiO_2 was amorphous.

To determine the optimum TiO_2 content on FAT for Cr(VI) analysis, the volume ratio of FA to TiO_2 in the range from 0.05 to 1 was investigated, and the results are shown in Fig. S2. The SERS intensity of Cr(VI) at 788 cm^{-1} which was attributed to $\nu_s(\text{Cr-O})$, the symmetric stretching vibrations of Cr(VI) was found to be similar (average 3938 ± 265 a.u.) on different FAT substrates. Meanwhile, SEM-EDS results shown in Table S1 indicate that the Ti atom ratio is stable in the range of 6.54–6.79% due to similar thicknesses of TiO_2 layers on different FAT substrates (Fig. S3). This result indicates that the volume ratio of FA to TiO_2 in FAT fabrication has almost no influence on Cr(VI) detection.

3.2. FAT for SERS detection of Cr(VI)

SERS spectra of Cr(VI) with concentrations ranging from 0.1 to 5 μM on FA substrates are shown in Fig. 2A. The enhancement factor (EF) was estimated by comparing the intensity of the primary peak at 788 cm^{-1} according to the equation

$$EF = (I_{\text{SERS}}/I_{\text{R}}) \times (C_{\text{R}}/C_{\text{SERS}});$$

where I_{SERS} and I_{R} are the intensities in the SERS and normal Raman spectra of Cr(VI), respectively, and C_{R} and C_{SERS} are Cr(VI) concentrations in normal and SERS samples related to the molecules adsorbed on the substrate, respectively [30]. The EF of the FA substrate for Cr(VI) was 3.8×10^5 with a detection limit of 1 μM (Fig. 2A, Table 1). After being coated with the 2–6 nm TiO_2 layer, the EF

Table 1

Detection of Cr(VI) on different SERS substrates.

Substrates	Detection Limit (μM)	Ref
PDDA-Au NPs	48.07	[11]
Cationic-coated Ag and Au	1.14	[12]
ARS- TiO_2 complexes	0.6	[13]
$\text{Fe}_3\text{O}_4/\text{Ag}$	0.1	[14]
FA	1	this work
FAT	0.05	this work

was improved to $4.2\text{--}9.3 \times 10^6$ with a detection limit of 0.05 μM (Fig. 2B, Table 1), which is an order of magnitude less than previously reported (Table 1).

To validate the effectiveness of the FAT SERS substrates, Cr(VI) was detected at different concentrations. The peak intensity at 788 cm^{-1} increased as the Cr(VI) concentration increased from 0.01 μM to 5 μM ($R^2 = 0.97$, Fig. 2C). The concentration-dependent response can be well described using the following curve fitting equation:

$$\frac{I}{C} = P + QI + RI^2,$$

where I_{SERS} is the SERS intensity of each Cr(VI) sample at 788 cm^{-1} . C is the concentration of Cr(VI), and P (5832.6), Q (−0.47), and R (-2×10^{-5}) are the fitting parameters [31,32]. The signal intensity increased in response to increasing the Cr(VI) concentration before reaching a plateau, most likely due to saturation of the SERS substrate “hot spots”. Error bars are estimated to illustrate the sample-to-sample variation of the SERS intensity. This observation

Fig. 3. (A) Selectivity of the FAT substrate toward Cr(VI) on the characteristic Raman band at 788 cm^{-1} in the presence of common ion species with a concentration of $1\text{ }\mu\text{M}$. (B) SERS intensity at 788 cm^{-1} for $1\text{ }\mu\text{M}$ Cr(VI) as a function of FAT storage time. The data points represent the average $\pm$ standard deviation for 25 randomly chosen points. Signal collection time = 1 s.

implies that the nanocomposite substrates have advantages for the quantitative analysis of Cr(VI).

The distribution of a local electric field was simulated with FDTD methods to estimate the intensities for FA and FAT (Fig. 2D, E). In agreement with our SERS observations, the FDTD results show that the EF increased from 1.0×10^4 on FA to 3.1×10^5 on FAT, which may be attributable to the SERS effect of TiO_2 [21,33]. In addition, the layer of TiO_2 has a strong adsorption ability which facilitates Cr(VI) enrichment on FAT surfaces.

To examine the selectivity of the FAT substrates, the interferences of each of 15 ions commonly encountered in natural waters were considered including Al^{3+} , As(III) , As(V) , Ca^{2+} , Cd^{2+} , Cu^{2+} , Hg^{2+} , K^+ , Mg^{2+} , Na^+ , Pb^{2+} , Sb(III) , Sb(V) , Cr(III) and Zn^{2+} . As shown in Fig. 3A, the average SERS intensity for Cr(VI) was $4028 \pm 358\text{ a.u.}$; whereas that for Mg^{2+} , the ion with the highest SERS response among the 15 coexisting ions, was only $239 \pm 11\text{ a.u.}$, which indicates that it contributes negligible interference toward Cr(VI) detection. These results illustrate that our FAT substrates have excellent SERS selectivity for Cr(VI) over other coexisting ions.

To study the reproducibility and uniformity of FAT by collecting Cr(VI) SERS spectra at 20 points that were randomly chosen on five samples, which were prepared using $0.1\text{ }\mu\text{M}$ 1 mL Cr(VI)-containing solution and 0.3 mg FATs substrate. The results in Fig. S4 show that evenly distributed hot spots on the FAT substrate. To further estimate the stability of the as-prepared FAT substrates, SERS measurements of $1\text{ }\mu\text{M}$ Cr(VI) were performed for 30 days (Fig. 3B). The result indicates that FAT has a good stability with an average SERS intensity of $4079 \pm 232\text{ a.u.}$ from 1 day to 30 days. The stability results illustrate that the FAT substrate can be used to monitor Cr(VI) with evident sensitivity lasting 30 days. This endurance is a result of the ability of the TiO_2 layer to protect nanoparticles from quick aggregation.

3.3. Identification of Cr(VI) in complex matrices

To investigate the SERS sensitivity for Cr(VI) in complex environmental matrices, a COPR sample and Cr(VI)-containing industrial wastewater were analyzed with the SERS platform. As shown in the box charts in Fig. 4, the average SERS intensities for COPR and wastewater were $3951 \pm 237\text{ a.u.}$ and $2838 \pm 281\text{ a.u.}$, respectively, corresponding to $107.4\text{ }\mu\text{M}$ and $65.3\text{ }\mu\text{M}$ Cr(VI). This result was comparable to the Cr(VI) content determined with ICP-OES ($98.1\text{ }\mu\text{M}$ and $65.0\text{ }\mu\text{M}$, respectively). These results confirm the

Fig. 4. Box charts of Raman Spectra of FAT substrate for COPR and wastewater samples. Signal collecting time = 1 s. The line within each notch box represent the median, while the lower and upper boundaries of the box indicate the first (25% percentile) and third (75% percentile) quartile, respectively. Error bars represent the 1.5-fold interquartile range.

capability of our FAT SERS platform for Cr(VI) quantification in environmental matrices.

3.4. Photo-reduction of Cr(VI)

With a 2–6 nm ultrathin layer of TiO_2 , our FAT SERS substrates can also be used as photo-reduction materials. The photo-reduction activity for Cr(VI) was estimated by monitoring the most intensive SERS band at 788 cm^{-1} . The decrease in peak intensity followed first-order kinetics of Cr(VI) decreasing with UV irradiation (Fig. 5A). This can be represented by the equation $I = I_0 e^{-kt}$, where I_0 (13012 a.u.) and I represent the initial SERS spectra and the SERS spectra of Cr(VI) at the exposure time, and k (0.0168 min^{-1}) is the linear plot of $\ln(I/I_0)$ versus the irradiation time. After 90 min, the SERS intensity of Cr(VI) decreased by almost 80%.

This photocatalytic activity of the FAT nanocomposites is mainly attributable to the charge transfer as shown in Fig. 5B. Under UV light (3.39 eV), electrons on FAT (band gap = 1.83 eV , inset of Fig. 5A) are transferred from the valence band to the conduction band,

Fig. 5. (A) Cr(VI) photocatalytic degradation with FAT as a function of time monitored using SERS characteristic peak intensity. Inset is $(\alpha h\nu)^{1/2}$ (α is the absorption coefficient) as a function of photon energy $h\nu$ for the determination of the band gap for the prepared FAT. (B) Schematic illustration of Cr(VI) photocatalytic degradation on FAT.

which generates electrons. This process is a result of Cr(VI) reduction [34,35].

4. Conclusion

We report here a core-satellite structured FAT substrate with homogeneous, stable, and highly efficient photo-reduction activity. Our experimental and FDTD simulation results show that decoration with a TiO_2 layer 2–6 nm thick enhanced the SERS sensitivity for Cr(VI) analysis with a detection limit of $0.05 \mu\text{M}$. In addition, FAT achieved fast photocatalytic degradation of Cr(VI) with first-order kinetics. This method provides an alternative platform for rapid field analysis and remediation of Cr(VI).

Acknowledgements

We acknowledge the financial support of the National Basic Research Program of China (2015CB932003), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB14020201), and the National Natural Science Foundation of China (41425016, 21337004, 21321004).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2016.10.048>.

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