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Flower-like self-assembly of gold nanoparticles for highly sensitive electrochemical detection of chromium(VI)

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Abstract

We report here the fabrication of a flower-like self-assembly of gold nanoparticles (AuNPs) on a glassy carbon electrode (GCE) as a highly sensitive platform for ultratrace Cr(VI) detection. Two AuNPs layers are used in the current approach, in which the first is electroplated on the GCE surface as anchors for binding to an overcoated thiol sol-gel film derived from 3-mercaptopropyltrimethoxysilane (MPTS). The second AuNPs layer is then self-assembled on the surface of the sol-gel film, forming flower-like gold nanoelectrodes enlarging the electrode surface. When functionalized by a thiol pyridinium, the fabricated electrode displays a well-defined peak for selective Cr(VI) reduction with an unusually large, linear concentration range of 10–1,200 ng L⁻¹ and a low detection limit of 2.9 ng L⁻¹. In comparison to previous approaches using MPTS and AuNPs on Au electrodes, the current work expands the use of AuNPs to the GCE. Subsequent functionalization of the secondary AuNPs by a thiol pyridinium and adsorption/preconcentration of Cr(VI) lead to the unusually large detection range and high sensitivity. The stepwise preparation of the electrode has been characterized by electrochemical impedance spectroscopy (EIS), scanning electronic microscopy (SEM), and IR. The newly designed electrode exhibits good stability, and has been successfully employed to measure chromium in a pre-treated blood sample. The method demonstrates acceptable fabrication reproducibility and accuracy.

Keywords

gold nanoparticles; self-assembly; glassy carbon electrode; sol-gel; thiol pyridinium; chromium detection

1. Introduction

Hexavalent chromium is a toxic, strong oxidizing agent. The wide use of chromium in industry has inevitably led to ecological impacts from Cr(VI) contamination, causing allergic dermatitis, as well as toxic, carcinogenic effects and mutagenesis in animals and humans [1–4]. There has thus been a growing interest in highly sensitive and selective assays for trace Cr determination. A number of sensitive techniques have been employed, such as atomic absorption spectrophotometry [5], plasma mass spectrometry [6], spectrofluorimetry [7], spectrophotometry [8], and chemiluminescence [9], but each of these

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Appendix A. Supplementary Data

Supplementary data associated with this article can be found in the online version.

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processes is time consuming and necessitates expensive equipments. Various sensor systems have also been reported [10–16]. Most of these systems, however, have either limitations in sensitivity, simplicity or the high cost of equipments as well.

Electrochemical methods have been considered desirable for the Cr(VI) determination, and they have demonstrated advantages including speed of analysis, good selectivity, and sensitivity [17–31]. A poly(4-vinylpyridinium)-coated platinum electrode was developed by Cox and Kulesza for Cr(VI) preconcentration in the polymer films, followed by determination with the lack of interference by metal cations [17]. In a flow injection analysis system, a polyaniline/polystyrene composite electrode was used as a detector to monitor Cr(VI) with a detection limit of 4 ng L^{-1} [18]. A self-assembled monolayer of pyridinium on the Au electrode surface for sensitive Cr(VI) detection has been developed by Turyan and Mandler [19]. We have developed 2- and 4-pyridinium-functionalized sol-gel films through electrodeposition at a glassy carbon electrode (GCE) surface for Cr(VI) detection in aqueous solution [20–23]. The narrow concentration ranges, however, significantly limit the practical applications. Mercury electrodes have also been used for the electrochemical detection of Cr(VI) [24,25]. While extremely sensitive, their applications are limited due to the toxicity of mercury. In an effort to develop alternative electrodes to mercury, bismuth-film electrodes (BiFEs) have been developed for Cr(VI) detection through catalytic adsorption stripping voltammetry (CAAdSV) [26–29]. However, the poor reproducibility of BiFEs is challenging for Cr detection at a low concentration, and a complexing ligand is needed for the process, adding to the complexity of the detection process. It is thus highly desirable to develop a system that is not only sensitive, selective, and reliable but also simple, practical, and economical in its operation.

Nanosized particles of noble metals, especially gold nanoparticles (AuNPs), have been studied extensively due to their attractive electronic, optical, and thermal properties as well as catalytic properties and potential applications over numerous science and medical fields [30–33]. AuNPs have been used in electrochemistry to develop highly sensitive nanodevices for analytical and bioanalytical applications because of their superior biological compatibility, excellent conducting capability, high surface-to-volume ratio and high surface energy. The introduction of AuNPs onto the electrochemical interfaces has infused a new vigor into electrochemistry, as AuNPs have successfully functioned as electron-conducting pathways between the electrochemically active targets and the electrode surface [34–41]. The amperometric detection of ultratrace amount of Cr(VI) has been developed based on AuNPs growing on a conducting substrate modified with sol-gel-derived thiol functionalized silicate network, but the detection limit was not low enough for Cr(VI) detection at the ng L^{-1} level [42].

With the aim of developing a sensitive platform for voltammetric Cr(VI) detection without a complexing ligand, two layers of AuNPs have been introduced to design a pyridinium-functionalized flower-like self-assembly of AuNPs for sensitive detection of ultratrace Cr(VI) (Fig. 1). The electroplating of gold formed the first AuNPs layer on the GCE surface, followed by the chemisorption of a sol-gel coating derived from 3-mercaptopropyl-trimethoxysilane (MPTS). Chemically produced AuNPs were then infiltrated into the three dimensional (3D) matrix by forming Au–S linkages, forming a flower-like self-assembly of AuNPs. The fabrication leads to a significantly enlarged Au electrode surface and expands the use of AuNPs to the GCE surface. To our knowledge, such a double-AuNPs-layer approach on the GCE surface has not been reported.

When positively charged pyridinium functional groups were attached to the AuNPs surface through Au–S bonds, ultratrace negatively charged HCrO_4^- was successfully accumulated on the electrode surface, leading to a low detection limit (2.9 ng L^{-1}) and a concentration

range (10–1,200 ng L⁻¹) that is much larger than those by other related electrodes [19–21]. This electrode was successfully used for the Cr(VI) detection in a pretreated blood sample.

2. Experimental

2.1. Apparatus and materials

Electrochemical measurements were carried out on a modulated potentiostat (CHI 650a, CH Instruments). A three-electrode configuration consisted of a modified GCE (3 mm in diameter, BAS Inc.), Ag/AgCl (saturated KCl solution, CH Instruments) and a platinum wire (CH Instruments) as working, reference and counter electrodes, respectively. Electrochemical impedance spectroscopy (EIS) was performed in 0.1 M KCl containing 5 mM [Fe(CN)₆]^{3-/4-}. Scanning electronic microscopic (SEM) images were obtained with a LEO 1525 field emission scanning electron microscope. Reflection-transmittance FT infrared spectroscopy (IR) was measured using a Thermo Scientific Nicolet™ iS™ 10 spectrometer.

The following chemicals were used as received: chromium standard solution (1000 mg L⁻¹, Fluka), MPTS (Gelest), 4-pyridineethanethiol hydrochloride (PET, TCI-EP, Japan), chloroauric acid (HAuCl₄, 99.99%, Aldrich), trisodium citrate (Aldrich), K₃Fe(CN)₆ (Aldrich), K₄Fe(CN)₆ (Aldrich), NaF (Certified ACS, Fisher), KCl (Certified ACS, Mallinckrodt). Ultrapure water from a Millipore water purified system (≥18 MΩ•cm, Barnstead) was used in all assays. Other reagents were of analytical grade and used as received. All glassware were soaked in 1 M nitric acid bath and thoroughly rinsed with deionized (DI) water before use.

Colloidal AuNPs were prepared by the reported method [40], and details are given in the supplementary materials (SM).

2.2. Preparation of pyridinium-functionalized flower-like self-assembly of AuNPs

Prior to use, GCEs were polished carefully to a mirror-like surface on a standard electrode polishing kit (CH Instrument) including a 1200 grit Carbimet disk, 1.0 and 0.3 μm alumina slurry on a nylon cloth, and 0.05 μm alumina slurry on a microcloth polishing pad. After polishing, GCEs were successively sonicated with deionized (DI) water, ethanol and DI water for 5 min each. The deposition of the first AuNPs layer was carried out by the method reported in the literature [41]. In brief, the GCE was put in 0.01 M K₃[Fe(CN)₆] solution containing 0.1 M KCl and scanned by cyclic voltammetry in the range from -0.2 to 0.6 V until a pair of well-defined redox peaks was observed. AuNPs were then electroplated on the GCE surface by immersing the electrode into a 0.2 g L⁻¹ HAuCl₄ solution and applying a constant potential of -0.2 V for 100 s. After being rinsed with acetone, ethanol and DI water, respectively, the AuNPs coated GCE was treated in a fresh piranha solution (H₂SO₄/H₂O₂, 7:3) for 5 min and then rinsed again with DI water. Finally, the AuNPs coated/modified GCE was kept under N₂ gas flow for subsequent use. This first AuNPs layer acts as anchors for binding to MPTS in the next step.

Caution: The piranha solution is corrosive and should be used with extreme caution and handled only in a small quantity—MPTS modification was carried out by soaking the electrode in a 21 mM solution of MPTS in ethanol for 10 min. The MPTS self-assembled on the surface of the AuNPs by forming Au←S bonds and, after hydrolysis of the sol-gel precursor, existed as a three dimensional (3D) porous silicate network with thiol tail groups (-SH) (Fig. 1) [43]. The MPTS-modified GCE was then immersed into a solution containing colloidal AuNPs for 24 h to form a self-assembly of the second AuNPs layer. The resulting electrode was then dipped into a 5 mM solution of 4-pyridineethanethiol

(PET) containing 0.5 M H₂SO₄ for 10 min to attach the pyridinium group to the electrode surface. The electrode is ready to accumulate hydrogen chromate (HCrO₄⁻) and analyze it. It should be pointed out that in the acidic solution, HCrO₄⁻ is the dominant species [19].

Various stages of the modification were prepared under the optimized conditions.

2.3. Measurement procedure

To carry out the voltammetric measurements for Cr(VI), the AuNPs self-assembled electrode was first put in 20 mL of 0.15 M fluoride buffered solution (pH 4.5) and stirred for 5 min under open-circuit potential [19]. After the accumulation, the determination of Cr(VI) was carried out by transferring the electrode to a Cr(VI) free solution (0.15 M NaF, pH 7.8) and performing cathodic stripping square wave voltammetry (CSSWV) from 0.35 to -0.2 V with frequency of 15 Hz, step potential of 4 mV and amplitude of 25 mV. Stirring at a high speed was required during the accumulation process but not during the stripping step. The electrode surface was regenerated between measurements by electrocycling in the potential range from 0.35 to -0.2 V in 0.1 M HClO₄ for the elimination of Cr(VI) from the electrode surface [19].

A porcine blood sample was pretreated using the advanced oxidation process (AOP) as described previously [44], and Cr in the sample was converted to Cr(VI) in the pretreatment. Prior to the analysis, the blood sample was diluted using 0.15 M NaF buffer (pH 4.5). Standard additions of 100 and 200 ng L⁻¹ Cr(VI) were added to the blood sample to a total volume of 20 mL.

3. Results and Discussion

3.1. Characterization of flower-like self-assembly of AuNPs on GCE

The preparation of the pyridinium-functionalized flower-like surface self-assembly of AuNPs on GCE consists of four steps, as shown in Fig. 1. EIS and SEM measurements were used to characterize the modification from each step. EIS is an effective method for probing the features of a surface modified electrode. In the terms of EIS, the semicircle portion at higher frequencies corresponds to the electron-transfer limited process and the linear portion at lower frequencies may be attributed to diffusion. The semicircle diameter equals the electron-transfer resistance, which depends on the dielectric and insulating features at the electrode/electrolyte interface [41]. Fig. 2 shows the EIS measurements of different electrodes including bare GCE, AuNPs/GCE, MPTS/AuNPs/GCE, AuNPs/MPTS/AuNPs/GCE, and PET/AuNPs/MPTS/AuNPs/GCE. The small semicircle diameter of the bare GCE shows a relatively small electron-transfer resistance (curve a). An almost straight line observed for AuNPs/GCE (curve b) indicates faster electron transfer kinetics of [Fe(CN)₆]^{3-/4-} on AuNPs/GCE. However, the presence of MPTS sol-gel overcoating on AuNPs/GCE surface remarkably increases the electron transfer resistance (curve c), indicating the larger obstruction effect of MPTS sol-gel layer on the flow of electrons. The secondary AuNPs are therefore introduced to the electrode surface and self-assembled onto the 3D silicate network. In comparison with MPTS/AuNPs/GCE, the semicircle diameter of AuNPs/MPTS/AuNPs/GCE was much smaller (curve d). This is contributed to the high electrical conductivity of secondary AuNPs, facilitating the electron transfer between the electrode and the self-assembled layers. As PET can partly resist the electron transfer of the electrode, a slight increase of the impedance was observed after the attachment of PET (curve e) to the surface of secondary AuNPs, which consequently does not affect the detection since the attachment of PET will facilitate the attraction of [Fe(CN)₆]^{3-/4-} ions and a similar effect should be at play for Cr(VI) through the self-assembled layer.

The SEM images of various stages of the modification under the optimized conditions are shown in Fig. 3. After the electrochemical deposition, AuNPs with diameters of 25–40 nm were formed and well distributed on the GCE surface (Fig. 3a). Compared to a gold disk electrode, AuNPs/GCE provides more surface area to chemisorb the thiol sol-gel precursor MPTS. A 3D porous structure indicated the successful formation of the MPTS sol-gel overcoating, which was full of thiol tail groups ($-SH$), on the first AuNPs layer (Fig. 3b). Then the 20-nm colloidal AuNPs were attached to the thiol groups present inside and on the surface of the silicate network, which was verified by both EIS (Fig. 2, curve c) and SEM (Fig. 3c). The second, flower-like AuNPs layer was used to improve the electron transfer and immobilize the pyridinium group. The diameter of the second AuNPs layer was slightly increased after being coated by the thiol-pyridium PET (Fig. 3d), but there was no obvious difference in the surface morphology.

IR spectra of the modified electrodes further confirmed the success of the step-by-step modification. Figs. 4a and b show the reflection-transmittance FT-IR spectra of the MPTS precursor and its monolayer on the surface of AuNPs. Bands at 802 and 1075 cm^{-1} originating from Si-O-C modes of the MPTS precursor are replaced by stretching absorption of broad Si-O-Si bands positioned at ca. 1100 cm^{-1} in the monolayer spectrum. Furthermore, the disappearance of the 1189 cm^{-1} band was observed due to OCH_3 groups corroborating hydrolysis of the precursor in the sol-gel process. The existence of free $-SH$ tail groups in the monolayer was verified by the S-H stretching band around $2600\text{--}2630\text{ cm}^{-1}$ in Figs. 4a and b. The peak frequencies for asymmetric and symmetric methylene (CH_2) stretching vibrations appear at 2918 and 2848 cm^{-1} , respectively (Fig. 4b). These results indicated the formation of a cross-linked silicate structure on the AuNPs surface [45]. IR spectra of pure PET and its monolayer on the surface of the second AuNPs layer were studied as well (Figs. 4c and d). After PET was self-assembled onto the AuNPs surface, the bands at 2980 , 3025 and 3080 cm^{-1} assigned to the C-H stretching of the ring disappeared. However, the bands at 2852 and 2921 cm^{-1} corresponding to the symmetric and asymmetric alkyl C-H stretching were observed before and after the self-assembly. These results indicate the chain disorder similar to the chains of short alkanethiols on gold due to the formation of $Au-S$ bonds [19] and accordingly imply the successful attachment of PET onto the surface of AuNPs.

3.2. Voltammetric behavior of different modified electrodes

It is worthwhile to compare the electroactivity of bare GCE (a, Fig. 5) and electrodes modified with (b) MPTS/AuNPs, (d) PET/AuNPs, (e) AuNPs/MPTS/AuNPs, (f) AuNPs, (g) PET/AuNPs/MPTS/AuNPs, and (c) the gold disk electrode modified with PET (Fig. 5). Bare GCE and MPTS/AuNPs/GCE did not show obvious electrochemical response to 1500 ng L^{-1} Cr(VI), probably because there are no active sites on the GCE surface to adsorb Cr(VI) and the MPTS network can largely suppress the electron transfer for Cr(VI) reduction on the electrode. A small current was found for Cr(VI) reduction on either PET/AuNPs/GCE or AuNPs/MPTS/AuNPs/GCE. The pyridinium group chemisorbs $HCrO_4^-$ by ion exchange, and it is possible that AuNPs can also show some electrocatalytic activity towards the reduction of Cr(VI) [45], providing a good reason for the small response to Cr(VI). Even though the detection performance of AuNPs/GCE was improved to some extent, the electrode designed for Cr(VI) detection in this investigation displayed the overall best behavior and in particular, a great improvement in the response to Cr(VI) reduction in comparison to PET/Au.

Two layers of AuNPs were successfully self-assembled on the GCE surface. Compared to the Au disk electrode, the first layer of AuNPs increased the surface roughness and greatly enlarged the effective surface area of AuNPs coated electrode, leading to the chemisorption of more MPTS. The more MPTS adsorbed, the more thiol tail groups are introduced to the

electrode surface, increasing the number of secondary AuNPs on the 3D silicate network. Finally, the functional pyridinium groups are attached onto the surface of secondary AuNPs, playing a very important role in the accumulation of Cr(VI). More AuNPs lead to more pyridinium groups present on the electrode surface, and consequently result in the best responsive detection of Cr(VI) among the various electrodes. It appears that the two layers of AuNPs greatly contribute to the improved performance of the designed electrode for Cr(VI) detection at low levels.

3.3. Analytical performance

The peak current and potential for the Cr(VI) reduction depend on the modification of the electrode. The pyridinium-functionalized, AuNPs-based electrode exhibited a typical voltammetric response for Cr(VI) reduction, presumably from Cr(VI) to Cr(III). It is interesting that the peak potential for Cr(VI) reduction was found to be at 0.08 V, negatively shifted from 0.18 V when the Au disk electrode was modified using only PET [19].

The optimization of other experimental conditions was discussed in detail in supplementary materials (SM). Afterward the performance of PET/AuNPs/MPTS/AuNPs/GCE toward the detection of Cr(VI) was tested by CSSWV. Fig. 6 displays the current response of the designed electrode towards Cr(VI) in the concentration range of 10–1,200 ng L⁻¹. PET/AuNPs/MPTS/AuNPs/GCE showed a well-defined voltammetric peak at ~0.08 V and the peak current proportionally increased with the increasing concentration of Cr(VI). It should be noted that a slight positive shift of the peak potential was observed for higher Cr(VI) concentration, which also occurred in the previous report [19]. The reason for this shift is not understood, but may be related to the exchange of fluoride by HCrO₄⁻ ions. The calibration plot showed a good linear relationship by using the peak current as a function of the Cr(VI) concentration with a correlation coefficient of 0.999 (Fig. 6 *inset*). The detection limit (LOD) of 2.9 ng L⁻¹ was calculated according to a signal-to-noise ratio of 3, which was comparable with those of previously reported Cr(VI) detection using electrochemical techniques [19,46,47]. Standard deviations of 3.1% (n = 3) for inter-group detection and 4.2% (n = 3) for outer-group detection, respectively, were obtained, indicating high sensitivity, better stability and reproducibility of the method for Cr(VI) reduction. Such a high sensitivity could be ascribed to the synergistic effect of the pyridinium-functionalized, flower-like self-assembly of AuNPs and the flower-like gold nanoelectrode. Moreover, this method showed a wide detection range of Cr(VI), probably as a result of the large AuNPs surface area. The detection here demonstrates that the current method could be used for reliable and accurate Cr(VI) measurement at ng L⁻¹ level in real samples. The electrode, once made, was used for at least fifteen measurements with no obvious decrease in peak current.

3.4. Interference

A major challenge for Cr(VI) detection in real samples is the elimination of interferences. In order to evaluate the performance of PET/AuNPs/MPTS/AuNPs/GCE toward Cr(VI) reduction in the presence of coexisting anions or cations including ClO₄⁻, NO₃⁻, BrO₃⁻, MoO₄²⁻, SO₄²⁻, Cr³⁺, Pb²⁺, Al³⁺, Cd²⁺, Fe³⁺, Cu²⁺, and Zn²⁺, the effect of these ions on the cathodic peak current of Cr(VI) reduction was examined (Fig. S2 in SM). The voltammetric response of the designed electrode towards 300 ng L⁻¹ Cr(VI) was first measured, and 500-fold excess of the coexisting ions was subsequently added into the supporting electrolyte. At pH 4.5, HCrO₄⁻ is the main form of Cr(VI) in the aqueous solution. As expected, no change in the voltammetric response of Cr(VI) was observed in the presence of various cations, as the positively charged ions such as Cr³⁺ and Cu²⁺ are repelled by the positive charge of pyridinium group on the electrode surface. It is interesting that the presence of negatively charged ions only showed minute interference toward Cr(VI)

reduction, implying that the preconcentration of Cr(VI) was not a simple ion-exchange process. Moreover, even MoO_4^{2-} with the similar structure and size did not exhibit obvious interference.

3.5. Blood sample analysis

The analytical reliability and practical application potential of the new electrode was evaluated by measuring Cr(VI) in a blood sample [44]. Chromium is an essential trace element for mammals (3–10 ppb in the blood), and it is bound to peptides [48]. Prior to the analysis, the blood sample was thus first pretreated by H_2O_2 and UV irradiation (Advanced Oxidation Process, AOP) by a method developed in our group [44], in order to decompose the organic and biological species in the sample and to free chromium. As a result, Cr in the blood was converted to Cr(VI) in the pretreatment. Standard addition method was employed and the CSSWV measurements were performed before and after the addition of 100 and 200 ng L^{-1} of Cr(VI) to the sample (Fig. 7). A well defined peak around 0.0 V was observed and increased proportionally with the Cr(VI) addition. A slight, negative shift of the peak potential might be caused by the background of the AOP-treated blood sample. The original concentration of Cr(VI) in the blood sample was found to be $6.9(0.5)\mu\text{g L}^{-1}$, which is consistent with the previously reported value [44], with a recovery of more than 93%, and with a relative error less than 5.3%. This result demonstrates the successful use of the new electrode for the detection of Cr(VI) in the blood samples with acceptable accuracy. More importantly, the residual H_2O_2 from the blood pretreatment did not cause obvious interference in the performance of the current electrode. This is an evidence of the accuracy and reliability of the new electrode for the applications in real samples.

4. Conclusion

The fabrication of a new flower-like self-assembly of AuNPs-modified electrode is reported here. After functionalization by a thiol pyridinium, the electrode was used successfully toward Cr(VI) preconcentration and subsequent analysis. At the electrodes, Cr(VI) was efficiently reduced at 0.08 V in the absence of a complexing ligand, which is ~ 100 mV less positive than that for conventional Au disk electrodes. The introduction of two layers of AuNPs significantly enhances the detection behavior of the electrode and makes measurement simple, highly sensitive and selective, and stable. It provides a very low detection limit and a large, linear response comparable with that based on a bismuth film electrode that requires the use of a complexing ligand to exhibit high sensitivity for Cr(VI) reduction. No interference was found for aqueous Cr(VI) detection with the coexisting ions. The AuNPs-based electrode was used successfully for the detection of Cr(VI) in AOP treated blood sample without interference by residual H_2O_2 . The current work provides both a new flower-like AuNPs electrode on the GCE surface and a method for highly sensitive and selective Cr(VI) detection.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Highlights

- Fabrication of a flower-like self-assembly of two AuNPs layers on a GCE
- Cr(VI) detection: 10–1,200 ng L⁻¹ concentration range; 2.9 ng L⁻¹ detection limit
- The 1st AuNPs layer on the GCE surface as anchors for a thiol sol-gel film
- The sol-gel film link the 1st AuNPs layer to the 2nd AuNPs layer
- Functionalization of the 2nd AuNPs layer by a thiol pyridinium for HCrO₄⁻ detection

Fig. 1. Schematic illustration of the fabrication of the pyridinium-functionalized flower-like self-assembly of AuNPs on GEC and the mechanism of the preconcentration and detection of Cr(VI) by the electrode: (a) electrochemical deposition of AuNPs as anchors for MPTS; (b) self-assembling of MPTS on the surface of the first AuNPs layer as a thiol sol-gel overcoating; (c) chemisorption of the second AuNPs layer on the thiol sol-gel overcoating; (d) attaching of PET onto the surface of the second AuNPs layer; (e) voltammetric response of the electrode toward Cr(VI) reduction.

Fig. 2. EIS of $0.01 \text{ M Fe(CN)}_6^{3-/4-}$ and 0.1 M KCl at (a) bare GCE; (b) AuNPs/GCE; (c) MPTS/AuNPs/GCE; (d) AuNPs/MPTS/AuNPs/GCE; (e) PET/ AuNPs/MPTS/AuNPs/GCE.

Fig. 3. SEM images of (a) AuNPs/GCE; (b) MPTS/AuNPs/GCE; (c) AuNPs/MPTS/AuNPs/GCE – The term “flower-like” is used to describe the distribution of AuNPs on the thiol MPTS sol-gel film; (d) PET/AuNPs/MPTS/AuNPs/GCE. The insert in (d) is in the same magnification as that in Fig 3c.

Fig. 4. Reflection-transmittance IR spectra of (a) MPTS, (b) MPTS chemisorbed on AuNPs/GCE, (c) PET and (d) PET attached on AuNPs/MPTS/AuPs/GCE.

Fig. 5. Graphical comparison of (a) bare GCE; (b) MPTS/AuNPs/GCE; (c) PET/Au; (d) PET/AuNPs/GCE; (e) AuNPs/MPTS/AuNPs/GCE; (f) AuNPs/GCE; and (g) PET/AuNPs/MPTS/AuNPs/GCE toward $1500 \text{ ng L}^{-1} \text{ Cr(VI)}$ detection.

Fig. 6. Voltammetric performance and the corresponding calibration plot (*inset*) of PET/AuNPs/MPTS/AuNPs/GCE toward Cr(VI) reduction in the concentration range from 10 to 1200 ng L^{-1} . Error bar: $n = 3$.

Fig. 7. CSSWVs of the blood samples spiked with (a) 0, (b) 100 and (c) 200 ng L⁻¹ Cr(VI).