

Electrochemical Determination of Chromium(VI) in River Water with Gold Nanoparticles–Graphene Nanocomposites Modified Electrodes

Trisna K. SARI,* Fumiki TAKAHASHI,* Jiye JIN,*† Rahmiana ZEIN,** and Edison MUNAR**

*Department of Chemistry, Faculty of Science, Shinshu University, 3-1-1 Asahi, Matsumoto, Nagano 390-8621, Japan

**Department of Chemistry, Faculty of Mathematics and Natural Science, Andalas University, Padang 25163, Indonesia

In this study, nanocomposites of ligand-free gold nanoparticles that are anchored onto the graphene surface (Graphene/AuNPs) were synthesized by a sonochemical method in a single reaction step. A highly sensitive amperometric sensor using Graphene/AuNPs is proposed for the determination of trace hexavalent chromium Cr(VI) in environmental water samples. Compared with a gold electrode, a glassy carbon electrode and a AuNPs modified glassy carbon electrode, the Graphene/AuNPs modified glassy carbon electrode exhibits the highest electrocatalytic activity and stability towards the reduction of Cr(VI), based on the results by cyclic voltammetry and electrochemical AC impedance studies. This study shows that the Graphene/AuNPs-based sensor can detect Cr(VI) with a low detection limit of 10 nM (~0.5 µg/L), a wide dynamic range of 0 to 20 µM ($R = 0.999$) and very good selectivity and reproducibility. The electrode is applied to the determination of Cr(VI) in river samples with satisfactory recovery values.

Keywords Gold nanoparticles–graphene nanocomposites, sonochemical synthesis, hexavalent chromium Cr(VI) determination, amperometric sensor

(Received August 22, 2017; Accepted September 19, 2017; Published February 10, 2018)

Introduction

In natural water, chromium exists in two thermodynamically stable oxidation states, trivalent chromium Cr(III) and hexavalent chromium Cr(VI). Cr(III) is relatively less toxic than Cr(VI) and plays an essential role in biological processes, whereas Cr(VI) is a strong oxidizing agent, which is about 100 – 1000 times more toxic than Cr(III) due to its carcinogenic and mutagenic properties.^{1,2} In Indonesia, chromium is extensively used in industries such as leather tanning, electroplating, cement, mining, production of paints and pigments, and wood preservation.³ Therefore, a reliable and convenient method for monitoring of Cr(VI) is significantly important in order to provide control of this highly toxic substance for human and environmental concerns. Although sophisticated analytical techniques, like atomic absorption spectroscopy, UV-Vis absorption spectroscopy, and inductively coupled plasma mass spectroscopy, are generally employed for the determination of trace Cr(VI) in environmental samples,⁴⁻⁸ they suffer from drawbacks in terms of cost of routine analysis and tedious procedure of sample preparation.

Recently, electrochemical sensors have been proven to be promising analytical tools due to advantages such as possibilities for miniaturization and portability, sensitivity, selectivity, and

cost-effective instrumentation, a number of the electrode materials and detection strategies have been reported for the electrochemical quantification of Cr(VI). Among them, gold material based electrodes have attracted increasing interest in the last decade because Cr(VI) reduction can occur at a much lower over-potential compared with other noble metals, like platinum. Welch and Compton studied the electrochemical catalytic properties toward the reduction of Cr(VI) at a gold electrode, and demonstrated that Cr(VI) can be directly detected at a polycrystalline gold electrode by voltammetry with a detection limit of 4.3 µM.⁹

To improve the analytical performance for Cr(VI) detection, considerable efforts have been devoted to the functionalization and modification of the nanoparticle, itself, and/or its support materials in the past decade. Gold nanoparticles (AuNPs) or nanostructured gold modified electrodes have been developed due to their favorable characteristics in the enhancement of electron-transfer processes with respect to the polycrystalline gold electrode.¹⁰⁻¹⁷ The graphene-based nanomaterials is also being used for electrochemical sensing applications with greater frequency because of unique properties, such as high conductivity, excellent mechanical property and large active surface area.¹⁸⁻²³ A modified electrode with AuNPs and graphene nanocomposites for the detection of Cr(VI) was first reported by Santhosh and coworkers.¹⁸ Such a nanostructured composite film facilitated the electron-transfer processes in the reduction of Cr(VI), leading to a 100-times Cr(VI) reduction activity compared to that of a gold electrode, although the detection

† To whom correspondence should be addressed.
E-mail: jin@shinshu-u.ac.jp

limit was not provided. In their approach, the electrodes were prepared with two-steps: *i.e.* 1) modification of polyvinylpyrrolidone protected graphene/chitosan film onto a gold electrode surface first, and followed by 2) electrodeposition of AuNPs onto the film.¹⁸ On the other hand, the methodology for the fabrication of nanocomposites involved the use of chemical stabilizers or surfactants, which may cause some cross chemical effects.²⁴ A further systematic investigation about the Cr(VI) detection at the AuNPs decorated graphene electrodes is particularly necessary.

Considering that surfactants-free AuNPs present an improved specific surface activity, due to the absence of surfactants or ligands on the surface, this work proposed an alternative strategy for synthesizing surfactants-free AuNPs anchored to graphene (Graphene/AuNPs) by sonochemical method. A novel electrochemical sensor was fabricated by the modification of Graphene/AuNPs onto glassy carbon electrodes (GCEs) by a simple drop casting method. The electrochemical properties of the electrode in the reduction process of Cr(VI) was comprehensively studied, through a comparison with a gold electrode, a glassy carbon electrode and an AuNPs modified glassy carbon electrode. The application of the sensor for the determination of trace Cr(VI) in river-water samples in Japan and Indonesia is reported.

Materials and Methods

Chemicals

Graphene oxide powder was purchased from Nanjing ICNANO Technology Company (Nanjing, China); $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ and 2-propanol were purchased from Wako Pure Chemical Industries (Osaka, Japan). The atomic absorption standard solutions (1000 $\mu\text{g/mL}$) of Cr(VI), Cr(III), Cu(II), Pb(II), Cd(II), Zn(II), Co(II) and Mn(II) were purchased from Nacalai Tesque (Kyoto, Japan). The standard stock solution of Fe(III) was prepared by dissolving an adequate amount of FeCl_3 (Wako, Osaka, Japan) in distilled water. Perchloric acid (HClO_4) was obtained from Nacalai Tesque (Kyoto, Japan). All chemicals were of analytical grade, and solutions were prepared with distilled water purified by a WS200 distillation system (Yamato Scientific Co., Tokyo, Japan).

Apparatus

All of the electrochemical measurements were carried out with a Model 900 electrochemical workstation (CH Instruments, USA) with a standard three-electrode system. A glassy carbon electrode (1.6 mm in diameter, BAS Japan) or a gold disk electrode (1.6 mm in diameter, BAS Japan) served as a working electrode, a platinum wire served as a counter electrode, and an Ag/AgCl reference electrode (RE-1, BAS Japan) served as the reference electrode. The UV-Vis absorption spectra were recorded with a Shimadzu UV-2550 spectrophotometer (Shimadzu, Japan). Scanning electron microscopy (SEM) images were obtained with a JEOL or JSM-7600F scanning electron microscope, operated at 15 kV. It was equipped with an energy dispersive X-ray (EDS) spectrometer.

Preparation of AuNPs and Graphene/AuNPs by sonochemical method

Figure 1 shows a schematic diagram of the experimental setup for the preparation of AuNPs and Graphene/AuNPs. The sonochemical reactor was made of cylindrical acrylic chamber of 6 cm inner diameter and was filled with distilled water. A lead zirconate titanate (PZT) transducer with 500 kHz

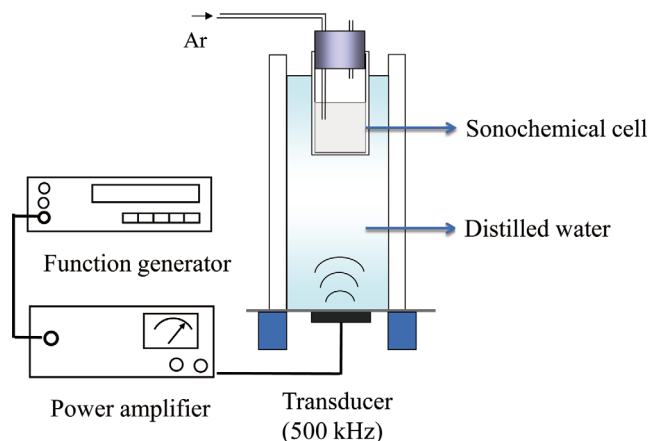


Fig. 1 Sonochemical reactor for the preparation of AuNPs and Graphene/AuNPs. A cylindrical glass vessel of 3 cm diameter was used as a sonochemical cell, which was placed above a transducer with a fixed position. In all experiments, the volume of the reaction solution in the cell was 10 mL.

(Q50PZT, Honda Electronics, Toyohashi, Japan) was mounted on a stainless-steel vibrational plate placed at the bottom of the reactor. The transducer was driven by an NF WF 1974 function generator and amplified by a THAMWAY T145-5015 amplifier, as was described in our previous study.²⁵ A cylindrical glass vessel of 3 cm diameter was used as the sonochemical cell, which was placed on the top of the chamber with a fixed position above the transducer, and was irradiated indirectly with ultrasound transducer. AuNPs were prepared by sonication of the cell containing 200 μM HAuCl_4 and 1% (v/v) 2-propanol. Prior to the sonication procedure, the solution was purged with argon (Ar) for about 20 min. Graphene/AuNPs nanocomposites were prepared by the sonication of an Ar saturated aqueous solution containing 200 μM HAuCl_4 , 1% (v/v) 2-propanol, and graphene (*ca.* 0.09 mg/mL). Before preparation, the graphene oxide powders were dispersed by sonication with an ultrasonic homogenizer Model VP-5S (20 kHz, TAITEC Co., Ltd., Japan).

Preparation of the modified electrodes

Before a modification, a glassy carbon electrode (GCE) was carefully polished with 0.3 and 0.05 μm Al_2O_3 powder until a mirror shiny surface appeared, and then rinsed with water and sonicated in double-distilled water for 3 min. A volume of 5 μL of Graphene/AuNPs/nanocomposites solution was added onto the clean GCE surface, and dried at room temperature for 1 h, and the electrode is denoted as Graphene/AuNPs/GCE. Figure 2 is a schematic of the electrode preparation. For comparison, an AuNPs coated electrode was also fabricated by dropping a volume of 5 μL of AuNPs solution onto the clean GCE surface, and is denoted as AuNPs/GCE.

River sample preparations

The water samples were collected from Metoba River (Matsumoto, Japan) and Gajah Wong River (Yogyakarta, Indonesia), respectively. Before the analysis, the samples were filtered with a glass filter (3G-4, Sansyo, Tokyo), and were then acidified with HClO_4 to a concentration of 0.1 M. The samples were pre-treated by a cation-exchange solid-phase extraction (SPE) cartridge (InertSep PRS, GL Sciences Inc. Japan) to remove the possible interference cations.

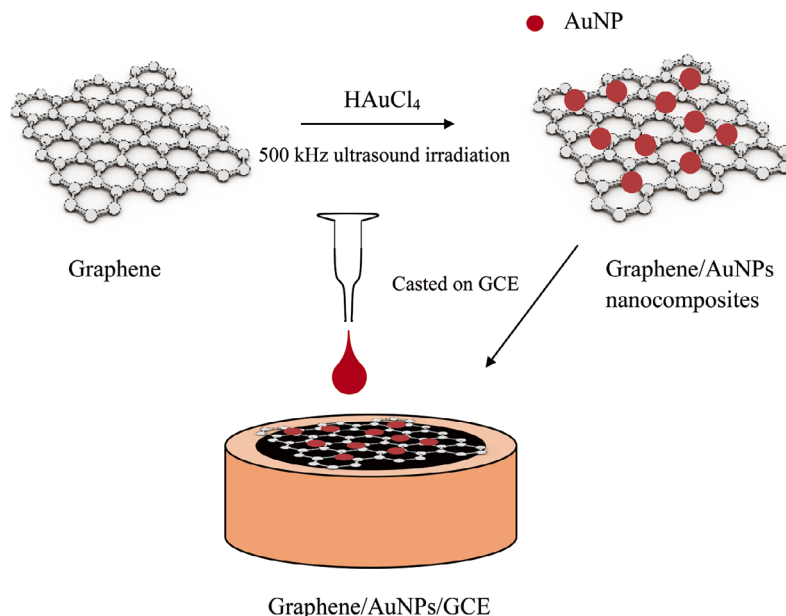
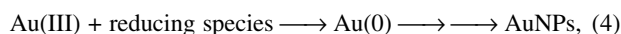
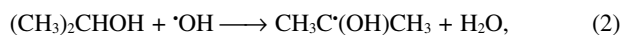


Fig. 2 Illustrations of the synthesis of Graphene/AuNPs nanocomposites and the electrode modification.

Results and Discussion

Sonochemical preparation of Graphene/AuNPs

Figure 3 shows SEM images of both AuNPs (a) and Graphene-AuNPs nanocomposites (b) prepared by the sonochemical method. It can be seen that small-size spherical particles (20 nm) of AuNPs were formed upon the sonication of an aqueous solution containing 200 μM HAuCl_4 and 1% (v/v) 2-propanol, and the absorption band around 525 nm due to plasmon resonance of AuNPs was observed from the representative UV/Vis absorption spectra of the colloid solutions. The sonochemical synthesis of AuNPs has been reported by several groups,^{26,27} in which a zero-valent gold atom, Au (0) was generated in according to the following sequence of reactions:



where Eq. (1) indicates the generation of high-energy species, such as $\cdot\text{OH}$ radicals and $\cdot\text{H}$ radicals from sonolysis of the water. In Eq. (2), the reaction of $\cdot\text{OH}$ with 2-propanol involves H-atom abstraction from C-H bonds, which leads to the production of a reductive 2-propanol radical $[\text{CH}_3\text{C}(\cdot\text{OH})\text{CH}_3]$.²⁷ Finally, Au(III) was reduced by a reaction with the reducing species, like $\cdot\text{H}$, $\text{CH}_3\text{C}(\cdot\text{OH})\text{CH}_3$, and H_2 , and formed AuNPs through several complex reaction steps. In our previous study,²⁵ it was demonstrated that the sonochemical reactor at a frequency of 500-kHz exhibited the highest sonochemical efficiency for $\cdot\text{OH}$ production. Thus, a sonochemical reactor with 500-kHz is considered to favor the preparation of AuNPs with high efficiency. With this approach, stable AuNPs are able to be synthesized without additional reducing agents or stabilizers.

The SEM image displayed in Fig. 3(b) shows the AuNPs with

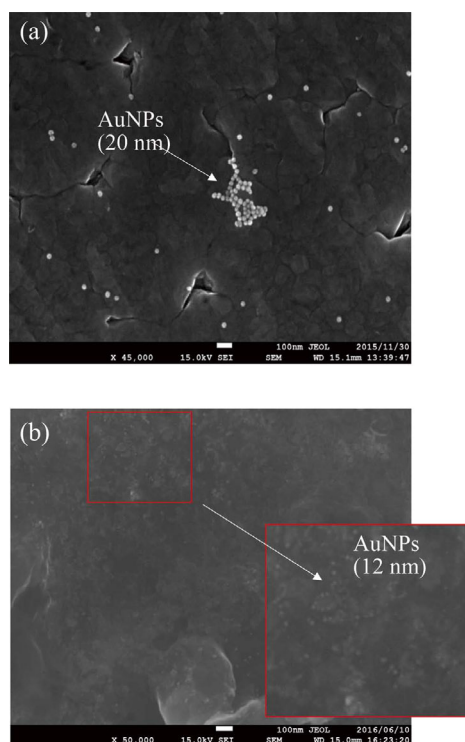


Fig. 3 SEM images of AuNPs (a) and Graphene/AuNPs nanocomposites (b). The inset in (b) is an image magnified at 10 times.

diameter around 12 nm deposited on graphene surface after the ultrasound irradiation. The results from energy-dispersive X-ray spectra confirmed gold elements in the nanocomposites. The presence of the oxygenated function groups on the graphene oxide are likely to provide binding sites for AuNPs attachment, through the electrostatic attraction of gold ions, hybrid materials could thus be produced in a short time by ultrasound.²⁸

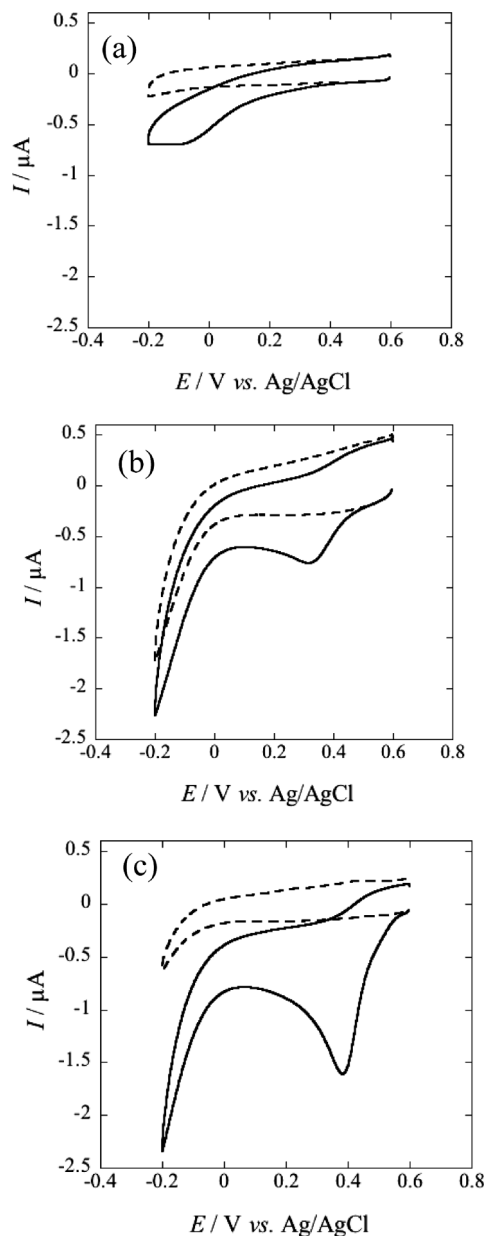


Fig. 4 CVs of a bare GCE (a), bare Gold (b), and Graphene/AuNPs/GCE (c), in 0.1 M HClO₄ in the presence of 50.0 μM Cr(VI). The potential scan rate was 0.1 V s⁻¹.

Electrocatalytic properties of Graphene/AuNPs/GCE towards Cr(VI) reduction

The electrochemical properties of the electrodes towards Cr(VI) reduction were first investigated by cyclic voltammetry (CV) in 0.1 M HClO₄ in the presence of 50.0 μM Cr(VI). Figure 4 shows the CVs at a bare GCE, an Au electrode, and a Graphene/AuNPs/GCE, respectively, with a scan rate of 0.1 V s⁻¹. Trace Cr(VI) ion presents as HCrO₄⁻ in an acidic solution employed.⁹ As depicted in Fig. 4, a bare GCE showed low current towards the reduction of Cr(VI) with a reduction potential about +0.06 V. At an Au electrode (Fig. 4), however, a well-defined peak due to the electrochemical reduction of Cr(VI) to Cr(III) was observed at more positive potential (+0.31 V), indicating the catalytic reductive property at the gold electrode surface.^{9,15} At the Graphene/AuNPs/GCE (Fig. 4), it reveals a similar voltammetric response, but provides much higher current densities, and reduction occurred at a more

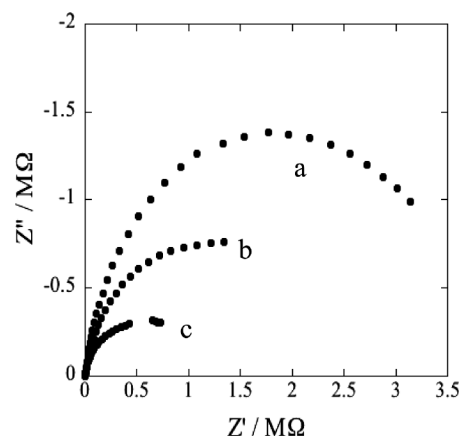


Fig. 5 Nyquist plots of a bare GCE (a), a gold (b), and Graphene/AuNPs/GCE (c), in 0.1 M HClO₄ containing 50.0 μM Cr(VI) at applied potentials of +0.1, +0.4 and +0.4 V vs. Ag/AgCl for a bare GCE, a gold, and a Graphene/AuNPs/GCE, respectively. The frequency range was 0.01 - 10000 Hz.

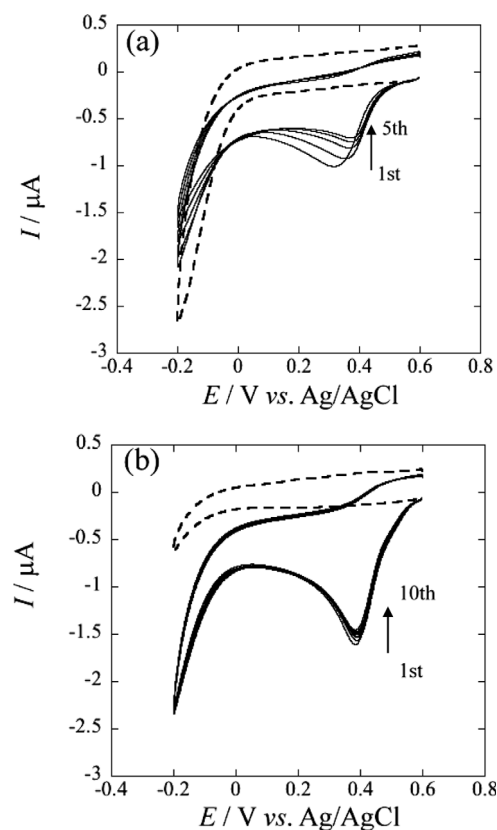


Fig. 6 Successive CV measurements of 50.0 μM Cr(VI) in 0.1 M HClO₄ at AuNPs/GCE (a) and Graphene/AuNPs/GCE (b), respectively. The potential scan rate was 0.1 V s⁻¹.

positive potential (+0.38 V), indicating a higher electrocatalytic activity of Graphene/AuNPs/GCE.

The electrochemical impedance spectroscopy (EIS) was performed to provide further insight into the charge-transfer resistances (R_{ct}) and the electrode kinetics under the conditions for the electrochemical reduction of Cr(VI) at a different electrode. Figure 5 shows Nyquist plots for a bare GCE (a), an Au electrode (b), and a Graphene/AuNPs/GCE (c) in 0.1 M HClO₄ containing 50 μM Cr(VI). The measurements were

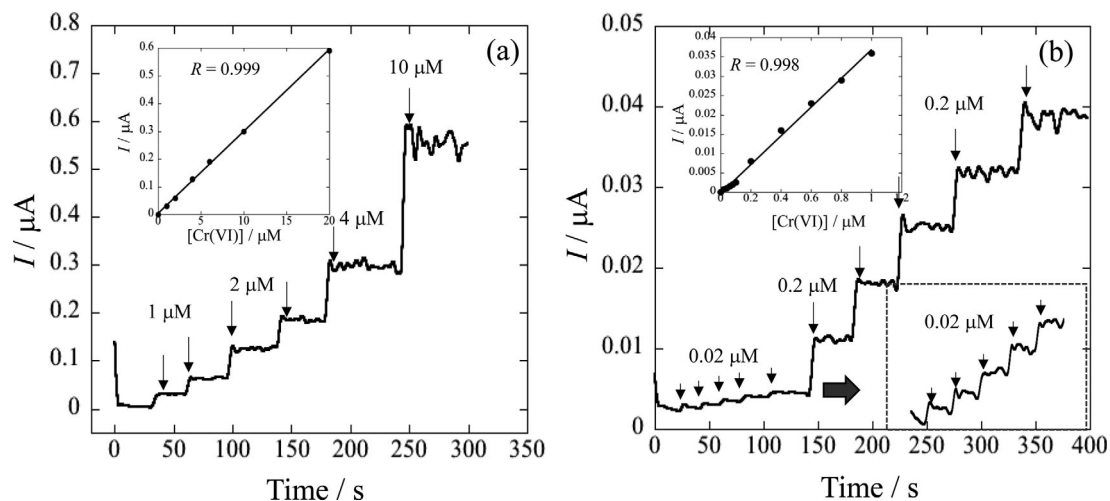


Fig. 7 Typical amperometric responses at the Graphene/AuNPs/GCE upon the successive addition of Cr(VI) into acutely stirred 0.1 M HClO₄ with different concentration levels. (a) Concentration range between 0 to 20 μM; (b) concentration range between 0 to 1.0 μM. The inset was the calibration curves. Applied potential: +0.20 V vs. Ag/AgCl; supporting electrolyte: 0.1 M HClO₄.

conducted at the equilibrium potentials in the frequency range of 0.01 – 10000 Hz with an amplitude of 5 mV, respectively. In the Nyquist plots of EIS, the diameter of a semicircle stands for the R_{ct} associated with the electrochemical reduction process of Cr(VI), based on the equivalent circuit model.²⁹ The values of R_{ct} were estimated to be $1.8 \times 10^4 \Omega/\text{cm}^2$ at a bare GCE, $1.2 \times 10^4 \Omega/\text{cm}^2$ at an Au electrode, and $6 \times 10^3 \Omega/\text{cm}^2$ at a Graphene/AuNPs/GCE, respectively. The results indicate that the Graphene/AuNPs/GCE provides the most electrocatalytic activity with a highly improved electrode kinetics.²¹ The surfactant-free Graphene/AuNPs may provide an improved specific surface area and well-exposed active sites of the adsorbed AuNPs, and consequently exhibited better catalytic properties.

The stability of Graphene/AuNPs/GCE was examined and compared with AuNPs/GCE by successive CV measurements of 50.0 μM Cr(VI) in 0.1 M HClO₄, as shown in Fig. 6. The reduction peak current decreased about 35% with a shift of peak potential at AuNPs/GCE after 5 potential scans, whereas, CVs at Graphene/AuNPs/GCE remained almost unchanged after 10 scans. The surfactant-free Graphene/AuNPs was considered to possess a stronger π - π stacking interaction with GCE, which leads to a strong immobilization effect. In other words, the Graphene/AuNPs/GCE can improve both the sensitivity and the stability for the detection of Cr(VI).

Amperometric responses at Graphene/AuNPs/GCE for Cr(VI) detection

The analytical performance of Graphene/AuNPs/GCE was evaluated by the constant-potential amperometric technique. Figure 7 shows the amperometric current responses of a Graphene/AuNPs/GCE at +0.20 V in a stirred solution of 0.1 M HClO₄ to the successive addition of Cr(VI) with concentration ranges from 1.00 to 20.0 μM (a) and from 0.020 to 1.00 μM (b). The currents showed a linear response in the concentration ranges of 0 to 20.0 μM and 0 to 1.00 μM with correlation coefficient values of 0.999 and 0.998, respectively. The detection limit was estimated to be 10 nM, or about 0.5 μg/L based on signal-to-noise ratio (S/N) of greater than 3. Graphene/AuNPs/GCE also offered excellent repeatability with a relative standard deviation (RSD) of about 1.70% for 5 repeated

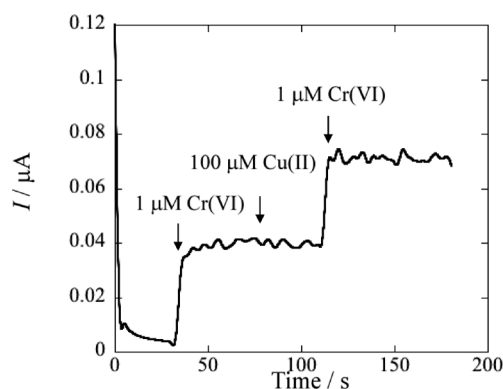


Fig. 8 Amperometric responses to 1 μM Cr(VI) and 100 μM Cu(II) at the Graphene/AuNPs/GCE in 0.1 M HClO₄. The detection potential was +0.20 V vs. Ag/AgCl. The samples were pre-treated with a cation exchange SPE cartridge.

measurements of 5.00 μM Cr(VI). Compared with previously published methods with gold based electrodes,¹⁰⁻¹⁸ the Graphene/AuNPs/GCE offers the advantages of a satisfied detection limit, convenient detection procedures and simple electrode preparation, which fulfills the requirement for potential practical applications.

Interferences

Under the optimum conditions, the influence of the interfering species, commonly present in environmental samples, was examined in a standard solution containing Cr(VI) at 1.00 M concentration. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error less than $\pm 5\%$ in the determination. It was found that 1000-fold amounts of Mn(II), Ni(II), and Cr(III) and 100-fold of Fe(III), Zn(II) and Co(II) did not show interference. At a detection potential of +0.2 V vs. Ag/Cl, 50-fold amounts of Pb(II), Cd(II) and Cu(II) showed an influence on the amperometric determination Cr(VI). Since hexavalent chromium existed as an anion HCrO_4^- , these interfering ions could be removed easily by using a cation-exchange SPE

Table 1 Determination and recoveries of trace Cr(VI) in river water samples

	Cr(VI) spiked/ μM	Found ^b / μM	Recovery, %	RSD ^c , % ($n = 3$)
Metoba River (Matsumoto, Japan)	0	N.D.	—	—
	0.1	0.101 ± 0.003	101	3
Gajah Wong River ^a (Yogyakarta, Indonesia)				
A	0	0.022 ± 0.001	—	3.3
	0.1	0.123 ± 0.002	101	1.6
B	0	0.018 ± 0.001	—	2.7
	0.1	0.120 ± 0.002	102	1.7
C	0	N.D.	—	—
	0.1	0.104 ± 0.001	104	0.9
D	0	N.D.	—	—
	0.1	0.104 ± 0.002	104	1.9
E	0	N.D.	—	—
	0.1	0.101 ± 0.002	101	2

a. Water samples were collected from a tanning industry location (A) 10 m (B) 100 m (C) 500 m (D) 700 m, and (E) 3000 m.

b. Mean of 3 measurements.

c. Relative standard deviation for $n = 3$.

N.D.: No detection.

cartridge. Figure 8 displayed the amperometric responses at the Graphene/AuNPs/GCE for samples of 1.00 μM Cr(VI) and 100 μM Cu(II) after treatment by a cation exchange SPE cartridge. No current response from Cu(II) could be detected.

Determination of Cr(VI) in river water samples

Determinations of trace Cr(VI) in river-water samples were conducted with Graphene/AuNPs/GCE. The water samples were collected from Metoba River (Matsumoto, Japan) and Gajah Wong River (Yogyakarta, Indonesia), respectively. There is a leather factory and a textile factory along Gajah Wong River, and the samples were collected in polyethylene bottles at the locations of (A) 10 m, (B) 100 m, (C) 500 m, (D) 700 m, and (E) 3000 m from the industrial region. After being filtered, the sample were acidified with 0.1 M HClO_4 , and then underwent the pretreatment solid phase extraction. Cr(VI) was analyzed using the standard addition method. To evaluate possible interactions by matrix, recovery experiments were also carried out by spiking the river samples with known amount of standard Cr(VI). The results of the analysis in these samples are listed in Table 1. No Cr(VI) was detected in Metoba River. However, trace Cr(VI) at levels of 0.022 and 0.018 μM were detected in the location of 10 and 100 m, respectively. Cr(VI) was not detected at locations far from 500 m. The recoveries and RSD values shown in Table 1 clearly demonstrate that Graphene/AuNPs/GCE did not record a measurable current response from any foreign substances. The proposed method can be potentially used for the determination and routine analysis of Cr(VI) in environmental samples.

Conclusions

In conclusion, the Graphene/AuNPs nanocomposites have been successfully synthesized by a sonochemical method, and a nanocomposite modified GC electrode. Graphene/AuNPs/GCE exhibits a high electrocatalytic activity for the reduction of Cr(VI) compared to a gold electrode and a glassy carbon electrode. The inherent stability, high sensitivity, low detection

limit, and low cost of analysis are the advantages of this method. The sensors were applied for the determination of trace levels of Cr(VI) in river samples in Indonesia.

Acknowledgements

This work was supported by JSPS KAKENHI Grant No. 16K05813.

References

- S. A. Katz and H. Salem, *J. Appl. Toxicol. Rev.*, **1993**, *13*, 217.
- R. M. C. Romero, M. C. Y. Biurrun, and M. P. B. Barrera, *Anal. Chim. Acta*, **1996**, *327*, 37.
- D. Mohan and C. Pittman, *J. Hazard. Mater.*, **2006**, *137*, 762.
- G. Vos, *Fresenius' Z. Anal. Chem.*, **1985**, *320*, 556.
- N. Unceta, F. Seby, J. Malherbe, and O. F. X. Donard, *Anal. Bioanal. Chem.*, **2010**, *397*, 1097.
- D. G. Themelis, F. S. Kika, and A. Economou, *Talanta*, **2006**, *69*, 615.
- B. Wen, X. Q. Shan, and J. Lian, *Talanta*, **2002**, *56*, 681.
- V. Gomez and M. P. Callao, *TrAC, Trends Anal. Chem.*, **2006**, *25*, 1006.
- C. M. Welch, O. Nekrassova, and R. G. Compton, *Talanta*, **2005**, *65*, 74.
- R. T. Kachosangi and R. G. Compton, *Sens. Actuators, B*, **2013**, *178*, 555.
- O. D. Renedo, L. R. Espelt, N. G. Astorgano, and M. J. A. Martinez, *Talanta*, **2008**, *76*, 854.
- B. Liu, L. Lu, M. Wang, and Y. Zi, *J. Chem. Sci.*, **2008**, *120*, 493.
- R. Ouyang, S. A. Bragg, J. Q. Chambers, and Z. L. Xue, *Anal. Chim. Acta*, **2012**, *722*, 1.
- H. D. Nguyen, T. T. L. Nguyen, K. M. Nguyen, T. A. T. Tran, A. M. Nguyen, and Q. H. Nguyen, *Am. J. Anal. Chem.*, **2015**, *6*, 457.
- M. C. Tsai and P. Y. Chen, *Talanta*, **2008**, *76*, 533.
- B. K. Jena and C. R. Raj, *Talanta*, **2008**, *76*, 161.
- W. Jin, G. Wu, and A. Chen, *Analyst*, **2014**, *139*, 235.
- C. Santhosh, M. Saranya, R. Ramachandran, S. Felix, V. Velmurugan, and A. N. Grace, *J. Nanotechnol.*, **2014**, *2014*, 1.
- Y. Wang, B. Song, J. Xu, and S. Hu, *Microchim. Acta*, **2015**, *182*, 711.
- A. Benvidi, A. D. Firouzabadi, M. M. Ardakani, B. B. F. Mirjalili, and R. Zare, *J. Electroanal. Chem.*, **2015**, *736*, 22.
- Y. Shao, J. Wang, H. Wu, J. Liu, I. A. Aksay, and Y. Lin, *Electroanalysis*, **2010**, *22*, 1027.
- S. X. Guo, S. F. Zhao, A. M. Bond, and J. Zhang, *Langmuir*, **2012**, *28*, 5275.
- C. Xu, X. Wang, and J. Zhu, *J. Phys. Chem. C*, **2008**, *112*, 19841.
- M. Haruta, *Catal. Today*, **1997**, *36*, 153.
- J. Jin, H. Kumeta, F. Takahashi, and Y. Asakura, *Chem. Lett.*, **2009**, *38*, 292.
- Y. Mori, N. Kitamoto, and K. Tsuchiya, *J. Chem. Eng. Jpn.*, **2005**, *38*, 283.
- K. Okitsu, M. Ashokkumar, and F. Grieser, *J. Phys. Chem. B*, **2005**, *109*, 20673.
- K. Vinodgopal, B. Neppolian, I. V. Lightcap, F. Grieser, M. Ashokkumar, and P. V. Kamat, *J. Phys. Chem. Lett.*, **2010**, *1*, 1987.
- A. J. Bard and L. R. Faulkner, "Electrochemical Methods: Fundamentals and Applications", 2nd ed., **2001**, John Wiley and Sons, New York.