

## Research Article

# Two Principles for Colorimetric Detections of Cr<sup>6+</sup> Using Polyurethane Foam—Gold Nanoparticles Composite

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**Abstract:** Two principles of leaching and precipitating for colorimetric sensing of hexavalent chromium using a composite of polyurethane foam with gold nanoparticles (PUF-AuNPs) with a smartphone and image processing were reported. The PUF-AuNP composites were exposed to different concentrations of hydrobromic acid (HBr) before taking a one-shot image and processing it to obtain a color value with ImageJ for a sample with triplicate results. In 0.05 M HBr, the leaching of AuNPs by oxidation would provide a linear calibration with yellow value =  $0.021[\text{Cr}^{6+}, \text{mM}] + 0.078$  ( $R^2 = 0.998$ ) for 0.5–5 mM with a limit of quantitation (LOQ) of 0.3 mM. In 1 M HBr, the amount of precipitate of Cr<sup>3+</sup>-bromide was proportional to the concentration of Cr<sup>6+</sup> with a linear range of 2–20 mM and a green value =  $-2.5[\text{Cr}^{6+}, \text{mM}] + 210$  ( $R^2 = 0.981$ ) with a limit of detection (LOD) of 0.6 mM. The precision was lower than 4% RSD with a good accuracy by % relative error. Various techniques, such as FT-IR, SEM, TEM, and EDS, confirmed the presented principles, and PUF-AuNPs. The PUF was readily synthesized in a lab using simple apparatuses like plastic cups and stirrer rods. AuNPs sorbed on PUF were obtained from the reduction of hydrogen tetrachloroaurate (III), which would be obtained from a low-cost gold leaf. Preliminarily, two proposed colorimetric sensors were tested for Cr<sup>6+</sup> assay in known aqueous samples with calculations in a calibration graph and the naked eye.

**Keywords:** polyurethane foam—gold nanoparticles composite (PUF-AuNPs), Cr<sup>6+</sup>, gold leaf, colorimetric sensing, leaching, precipitation

## 1. Introduction

Hexavalent chromium (Cr<sup>6+</sup>) is one of the most toxic metals. Cr<sup>6+</sup> can cause primary derma allergy and sensitization. Some cancers are also established from long-term obtaining<sup>1</sup>. The Pollution Control Department of Thailand legally allows the amount of Cr<sup>6+</sup> to be up to 50 ppb in water (groundwater, wastewater, tap water, and seawater)<sup>2</sup>.

Some conventional instruments for the determination of Cr<sup>6+</sup> can be used, such as the inductively coupled plasma mass spectrometer (ICP-MS)<sup>3</sup> and the UV-Visible spectrometer<sup>4–8</sup>. Even though high precision and low detection limits are the main strengths, the unaffordable price is a considerable challenge.

To overcome these drawbacks, there were various reports to minimize cost and obtain a reasonable detection limit, for example, electrochemical sensors<sup>9,10</sup>, colorimetric sensors with image processing<sup>11–13</sup>, and naked eyes<sup>14,15</sup>.

Due to noticeable color change and good stability, functionalized AuNPs with various reagents and materials have been applied using UV-Visible spectrophotometer and image processing based on several principles for the colorimetric detection of  $\text{Cr}^{6+}$ . Some of those were based on the aggregation of AuNPs after exposing  $\text{Cr}^{6+}$ <sup>4,7,8,14–17</sup>. Maleic acid functionalized with AuNPs accumulated after interaction with  $\text{Cr}^{6+}$ . The color of functionalized AuNPs changed from red wine to grey<sup>16</sup>. In some previous works, the leaching of AuNPs in the HBr medium would reduce the amount and size of AuNPs, and the color intensity or shade was changed<sup>6,11,12</sup>. Because of instability, the gold nano-double cone and silver nanorod were dissolved when presented in HBr acid.  $\text{Cr}^{6+}$  would oxidize the leached metals to obtain AgBr and  $\text{AuBr}^{2-}$  which reduced the size of nanoparticles. The color of nanoparticles changed from orange to pink-purple, which was proportional to the amount of  $\text{Cr}^{6+}$ <sup>12</sup>. Using a catalyst has also been reported in recent years<sup>13,18</sup>. A copper-based MOF nanozyme was a catalyst that would oxidize TMB as a chromogenic reagent. The electron was transferred to  $\text{Cr}^{6+}$ , which became  $\text{Cr}^{3+}$ . The greenish blue was developed for colorimetric detection<sup>18</sup>. Even though, these works provided a good sensitivity and clear color changes, employing AuNPs as a solution for colorimetric detection needed a stabilizer to control its stability over time as well as size and dispersion<sup>4,6,7,11–15</sup>. Incubation in a fridge is inevitable.

Synthesis of AuNPs on solid support could provide good stability and allow the preparation in a mild condition. Polyurethane foam (PUF)<sup>19,20</sup> and modified clay<sup>21</sup> allowed AuNPs to be sorbed on it via the reduction of hydrogen tetrachloroaurate (III) solution at room temperature.  $\text{Au}^{3+}$  was kindly reduced to  $\text{Au}^0$ NPs by sodium borohydride. However, using a commercially available hydrogen tetrachloroaurate (III) solution for AuNPs preparation is expensive.

In recent years, our group has used polyurethane foam (PUF) in a part of a colorimetric sensor with a simple device such as a smartphone with image processing, and a handy spectrometer, such as a monolithic PUF-4-(2-pyridylazo)resorcinol (PAR) for lead assay with a smartphone detection<sup>22</sup> and positively charged foam for removing iron and copper before nickel colorimetric detection<sup>23</sup> due to low costs, high stability, high surface area, tolerance, simplicity, and ease of preparation.

Interestingly, using AuNPs modified with PUF based on leaching and precipitation mechanisms for colorimetric  $\text{Cr}^{6+}$  sensing with the smartphone and image processing has yet to be reported. A low-cost pure gold leaf was available in local markets in Thailand which can be extracted to obtain a hydrogen tetrachloroaurate (III) solution.

This work proposed the exploitation of a polyurethane foam–gold nanoparticles composite (PUF-AuNPs) with a smartphone for colorimetric sensing of  $\text{Cr}^{6+}$  based on leaching and precipitation. Hydrogen tetrachloroaurate (III) would be obtained from a low-cost gold leaf before reducing to AuNPs to be sorbed on PUF. The aimed detection was exposed to the  $\text{Cr}^{6+}$  solution in the presence of different hydrobromic acid concentrations before taking a one-shot image to obtain one standard calibration with at least four samples in triplicate. The two-color shade change was based on two mechanisms: the leaching of AuNPs and the precipitate of  $\text{Cr}^{3+}$ -bromide with two linear calibrations. The proposed work was low-cost and easy to be prepared in mild conditions. Various techniques, for instance, UV-visible spectroscopy, Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDS) have been applied to confirm the presented composites and two principles for colorimetric  $\text{Cr}^{6+}$  detection.

## 2. Experimental

### 2.1 Apparatus

Digital images of oxidized gold nanoparticles on PUF were taken using a smartphone (iPhone 8 plus, Apple, California, United States). Yamera application was chosen to fix the settings of the smartphone camera as follows; offset: 0.0, ISO: 22, shutter speed: 1:55, and bias: 0.8. A light-controlled photograph box (UDIOBOX UDIO BIZ 40 cm × 40 cm × 40 cm, Bangkok, Thailand) was used<sup>22,23</sup>. The confirmations of present composites and two principles for colorimetric  $\text{Cr}^{6+}$  detection were achieved by light absorption (GetSpec-2048-SPU Fiber-Optic Spectrometer, Avantes, Colorado, USA), FT-IR (Nicolet 6700, Thermo Scientific, Massachusetts, USA), SEM (JSM-7800FPRIME Schottky Field Emission Scanning Electron Microscope, JEOL, Tokyo, Japan), TEM and EDS (JEM-2010 Transmission Electron Microscope, JEOL, Tokyo, Japan). ImageJ software (National Institutes of Health, Bethesda, Maryland, USA) was chosen to process

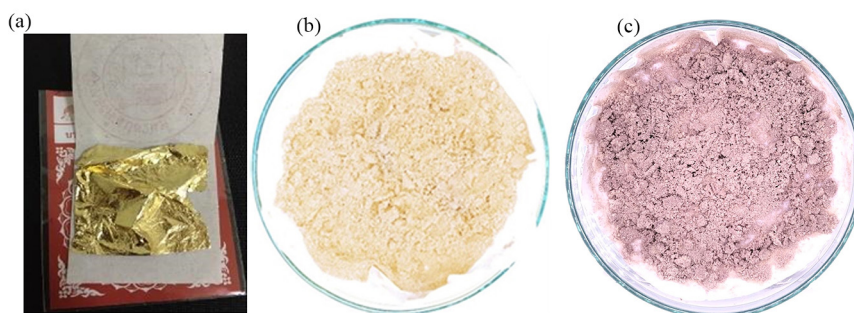
the images. A digital pH meter (METTLER TOLEDO, Greifensee, Switzerland) was employed to measure the pH of solutions.

## 2.2 Reagents and solutions

The analytical grade of all chemical reagents was used in this work. Deionized water was used to prepare the solutions. A 1 M stock solution of  $\text{Cr}^{6+}$  was prepared by dissolving  $7.340 \times \text{g}$  of  $\text{K}_2\text{Cr}_2\text{O}_7$  (Loba Chemie, Mumbai, India) to 50 mL with water in a volumetric flask. Working solutions with various concentrations of  $\text{Cr}^{6+}$  were prepared daily by proper diluting them with deionized water. An aqua regia acid was achieved by mixing 5 mL of 37% hydrochloric acid and 1.2 mL of 67% nitric acid, then making up to 100 mL with deionized water.

## 2.3 Preparation of hydrogen tetrachloroaurate (III)

A gold leaf with a purity of 99.99% (Chang, Thailand) (Figure 1a) was bought from the local market and weighed approximately 0.05 g before digestion with 25 mL of aqua regia acid, followed by heating at  $75^\circ\text{C}$  for 4 h with vigorous stirring to get a complete dissolution of gold leaf and eliminate the excess of nitric and hydrochloric acids. A treated  $\text{HAuCl}_4$  solution would be obtained. After cooling down at room temperature, the crude mixture was filtered, and the filtrate was adjusted to a volume of deionized water. A clear yellow solution of approximately 6 mM  $\text{HAuCl}_4$  was obtained. The treated gold solution was diluted with deionized water before daily use.



**Figure 1.** A gold leaf for hydrogen tetrachloroaurate (III) preparation (a), PUF (b), and PUF-AuNPs (c)

## 2.4 Preparation of polyurethane foam-borohydride (PUF-BH<sub>4</sub><sup>-</sup>)

In a plastic cup, the polyurethane foam (PUF) (Figure 1b) was polymerized by mixing methylene diphenyl diisocyanate (MDI; IRPC, Thailand) with polyol (polyether; IRPC, Thailand) in a ratio of 2:1<sup>22</sup>. The mixture was stirred to complete homogeneity and gave time to obtain the softened foam. The PUF was grounded into small pieces, before using a sieve of 180–600  $\mu\text{m}$  size. A 5 g PUF powder was stirred with 0.01 M sodium hydroxide, 0.01 M sodium borohydride, and 0.1 mM CTAB solution, respectively, at 110 rpm for 30 min, followed by filtration, washing with deionized water, and drying at room temperature to obtain PUF-BH<sub>4</sub><sup>-</sup><sup>19,20</sup>.

## 2.5 Preparation of composite of polyurethane foam with gold nanoparticles (PUF-AuNPs)

An approximate 5 g PUF-BH<sub>4</sub><sup>-</sup> was weighted and stirred with diluted hydrogen tetrachloroaurate (III) solution pH 6 at 110 rpm for 30 min. After that, the filtration and washing by deionized water were carried on before drying at  $110^\circ\text{C}$  for 30 min to give the final product of red-purple PUF-AuNPs (Figure 1c)

## 2.6 The procedure for the hexavalent chromium assay

A certain amount of PUF-AuNPs were exposed with a specific volume of an analyte solution in 0.05 M (first procedure) or 1 M HBr (second procedure) for 30 min at 110 rpm. It was then filtered and washed with deionized water. The solid residue was placed onto a well and left until dry. A one-shot with Image processing of the obtained solid was performed via ImageJ to provide a color value. The standard calibration was plotted between  $[\text{Cr}^{6+}, \text{mM}]$  vs. the signal of image property. The amount of  $\text{Cr}^{6+}$  in the sample was then calculated for all procedures or observed with the naked eye for the second procedure.

## 3. Results and discussion

### 3.1 Synthesis of PUF-AuNPs

In the presented work, the PUF was synthesized based on the previous work, briefly, methylene diphenyl diisocyanate with a polyol in a ratio of 2:1<sup>22</sup>. The positive charges of  $-\text{NH}$  groups at urethane bonds were advantageous from this PUF due to using MDI instead of TDI. Commercially, TDI consists of one aromatic ring, whereas MDI possesses two, which makes electron transportation easier. For this reason, negative charges of borohydride ions were readily sorbed on PUF at the positive part of  $-\text{NH}$  groups.  $\text{PUF-BH}_4^-$  was stirred with the prepared hydrogen tetrachloroaurate (III) from the gold leaf to obtain PUF-AuNPs. A cheaper price than a commercial hydrogen tetrachloroaurate (III) is predominant. A gold leaf sheet (approximately 0.05 g) could be bought from general local markets in Thailand for  $\sim 1.4$  \$ per each. The reduction method of  $\text{Au}^{3+}$  ion on the PUF surface was carried out under mild conditions to obtain AuNPs sorbed on PUF. At the same time, preparing AuNPs solution required an exact temperature of around  $100^\circ\text{C}$ <sup>24</sup> before sorption on PUF. The proposed PUF-AuNPs allowed a long lifetime and could be kept at room temperature.  $\text{AuCl}_4^-$  ( $\text{Au}^{3+}$ ) would be reduced by  $\text{BH}_4^-$  to be given  $\text{Au}^0$ NPs and sorbed on the PUF surface. PUF also plays a solid-phase stabilizer with others, namely, NaOH and CTAB, to control the charge of  $\text{Au}^0$ . PUF consists of polar and non-polar parts that readily allow  $\text{Au}^0$  to sorb.

### 3.2 Effect of hydrogen tetrachloroaurate (III) concentration

The concentration of hydrogen tetrachloroaurate (III) ( $\text{HAuCl}_4$ ), prepared from the gold leaf, was an important parameter to obtain a consistent color of AuNPs sorbed on PUF and good sensitivity for color change. An excess amount of  $\text{HAuCl}_4$  was required. The effect of  $\text{HAuCl}_4$  concentration was investigated and diluted to a series of the concentrations at 0.05, 0.1, 0.2, 0.5, and 1 mM (Figure 2). A 5 g  $\text{PUF-BH}_4^-$  powder was stirred in different  $\text{HAuCl}_4$  concentrations with a particular volume from 0.05–1 mM then obtaining PUF-AuNPs. The purple value was a color channel that related to the color of AuNPs, from image processing provided no significant difference after 0.5 mM  $\text{HAuCl}_4$ , indicating the excess amount of AuNPs sorbed on PUF. Conversely, 0.05–0.2 mM  $\text{HAuCl}_4$  produced lower signals of purple value, showing a smaller amount of AuNPs sorbed on PUF. For convenience, a concentration of 0.6 mM was chosen for the composite preparation.

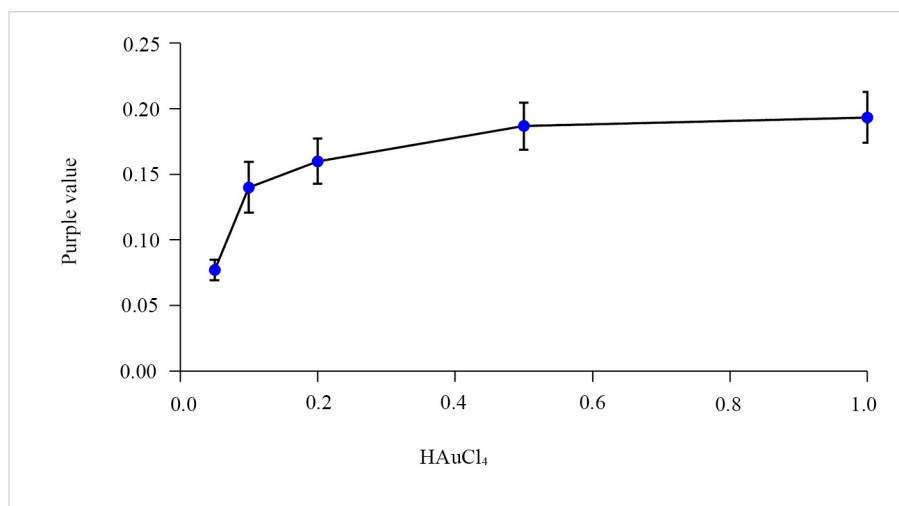


Figure 2. Effect due to hydrogen tetrachloroaurate (III) concentration

## 4. Characterizations

### 4.1 Fourier transform infrared spectrometer, FT-IR

From the IR spectra of PUF (Figure 3),  $\text{-NH}$  stretching and bending at  $3341$  and  $1510\text{ cm}^{-1}$ ,  $\text{-CO}$  and  $\text{-CN}$  stretching in  $1708$  and  $1210\text{ cm}^{-1}$  indicated the urethane bond of PU. However,  $\text{NCO}$  stretching still appeared due to using the amount of MDI ( $\text{-NCO}$ ) higher than Polyol ( $\text{-OH}$ ) as the ratio of 2:1. Percent transmission of many groups, such as  $\text{-CO}$  stretching at  $1708\text{ cm}^{-1}$  from PUF-AuNPs and PUF-AuNPs after exposing a solution of  $\text{Cr}^{6+}$  in 1 M HBr, dramatically decreased than PUF. This might be relevant to the interaction between sorbed AuNPs or the sediment of  $\text{Cr}^{3+}$ -bromide with PUF. Nonetheless, the difference between them was scarcely clear.

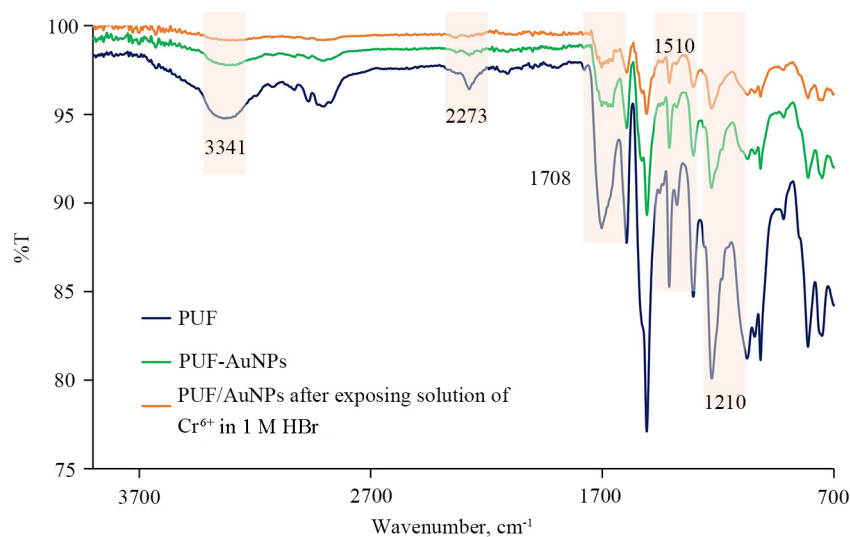


Figure 3. IR spectra of PUF (blue), PUF-AuNPs (green), and PUF-AuNPs after exposing a solution of  $\text{Cr}^{6+}$  in 1 M HBr (orange)

## 4.2 Optical fiber spectrometer

Scanning wavelength from 300–950 nm (Figure 4), PUF-AuNPs highly absorbed at 520 nm, which accorded to its color. This confirmed that AuNPs successfully sorbed on PUF.

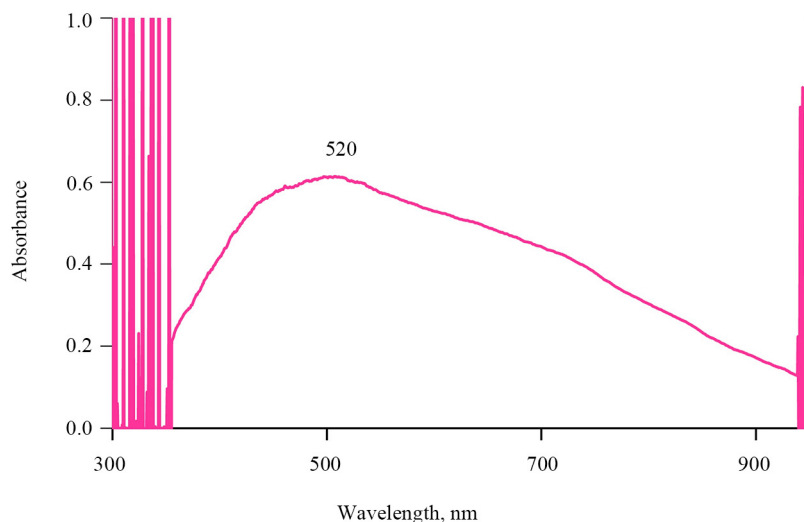
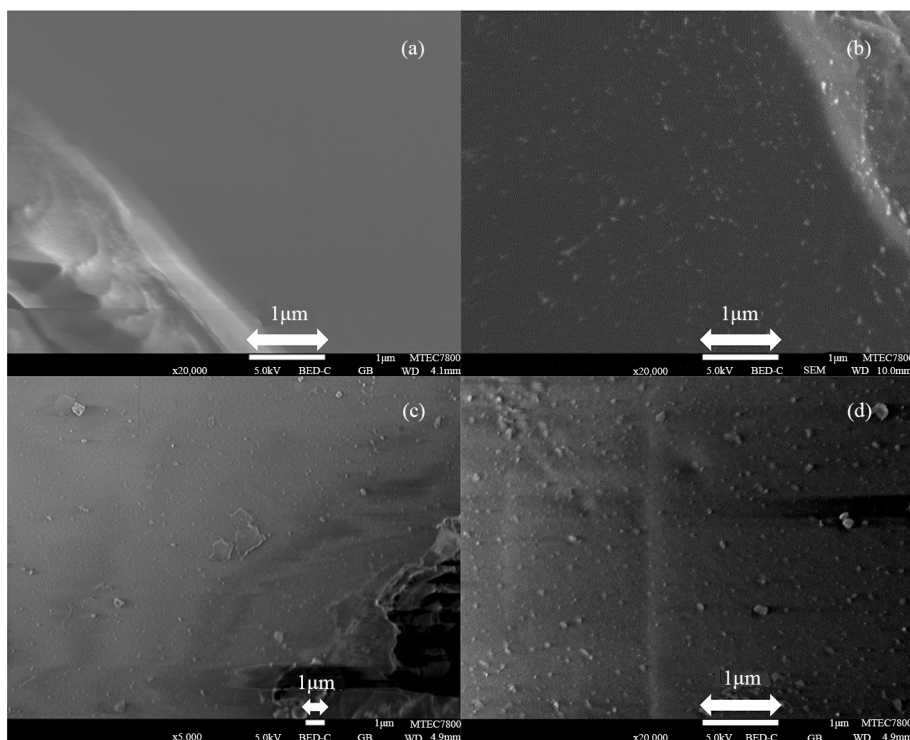


Figure 4. Absorption spectrum of PUF-AuNPs

## 4.3 Scanning electron microscope (SEM)

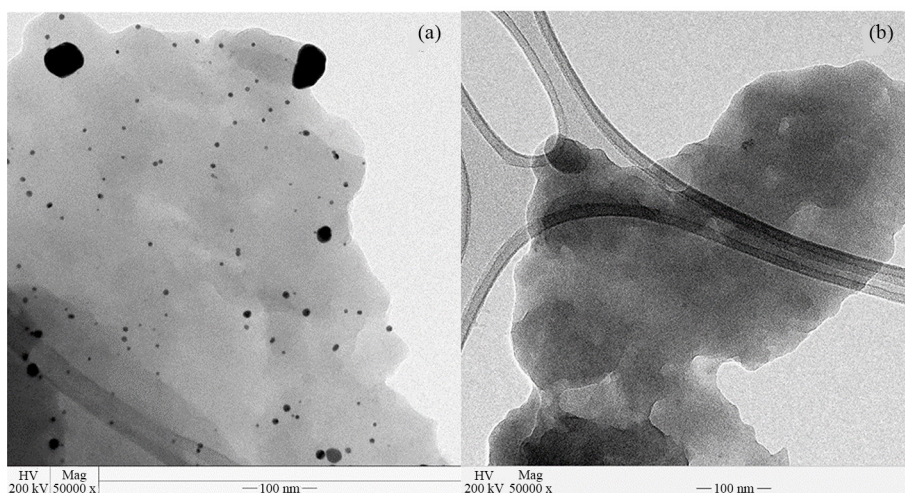
Each dried powder sample was coated with carbon paint. The backscattered electron mode in SEM was chosen and illustrated a smooth surface of PUF (Figure 5a) at 20,000 $\times$ . Unlike PUF-AuNPs (Figure 5b), it would be composed of abundant white spots indicating AuNPs. This implied the achievement of the PUF-AuNPs composite preparation. After PUF-AuNPs were exposed to  $\text{Cr}^{6+}$  in the presence of 1 M HBr, the PUF depicted flake-like, small sediments and rough surface at 5000 $\times$  and 20,000 $\times$ , which might accord to the precipitate of  $\text{Cr}^{3+}$ -bromide (Figure 5c,d).



**Figure 5.** SEM images of (a) PUF, 20,000 $\times$ ; (b) PUF-AuNPs, 20,000 $\times$ ; (c) PUF-AuNPs after exposure to  $\text{Cr}^{6+}$  in the presence of 1 M HBr, 5000 $\times$  and (d) 20,000 $\times$

#### 4.4 Transmission electron microscopy (TEM)

A solid support of rubber band-like Holey Carbon Cu-Grid was placed by each specimen. The results from TEM were synchronously related to SEM. The TEM image of PUF-AuNPs (Figure 6a) shows the distribution of dark particles on the grey PUF boundary depicted of AuNPs with an average size of  $6 \pm 3$  nm ( $n = 100$ ). Various apparent colors of AuNPs depend on their sizes and shapes. The obtained size of the circle of AuNPs is accorded to the red-purple color of AuNPs on PUF, and the absorption wavelength is 520 nm which is related to other works<sup>25-27</sup>. PUF-AuNPs were exposed to  $\text{Cr}^{6+}$  in the presence of 1 M HBr (Figure 6b). Then, AuNPs noticeably disappeared, and the PUF was covered with a thick matter, which might be the precipitate of  $\text{Cr}^{3+}$ -bromide.



**Figure 6.** TEM images of (a) PUF-AuNPs, 50,000 $\times$ ; (b) PUF-AuNPs after exposure to  $\text{Cr}^{6+}$  in the presence of 1 M HBr, 50,000 $\times$

#### 4.5 Energy-dispersive X-ray spectroscopy (EDS)

The EDS technique was used to identify the elements and indicate stoichiometry. C and Au were found in the spectrum (Figure 7a). This confirmed the successful preparation of PUF-AuNPs. The precipitate on PUF-AuNPs after exposing  $\text{Cr}^{6+}$  in the presence of 1 M HBr was investigated. The EDS spectrum (Figure 7b) consisted of C, O, and Si, which implied the components PUF, such as C and O atoms from the urethane bond and PUF's skeletons and Si atom from adding of silicone oil in the step of PUF synthesis<sup>22</sup>, while Cr and Br were the components of the precipitate. O and Si atoms were not observed in PUF-AuNPs. This might imply the interaction of these atoms and AuNPs. From Table 1, at atom (%), the ratio between Cr:Br was equal to 1:3. This should be the empirical formula of  $\text{CrBr}_3$ . The obtained EDS spectra for the claimed  $\text{CrBr}_3$  also agreed with the EDS spectra of a single crystal  $\text{CrBr}_3$ <sup>28</sup>.

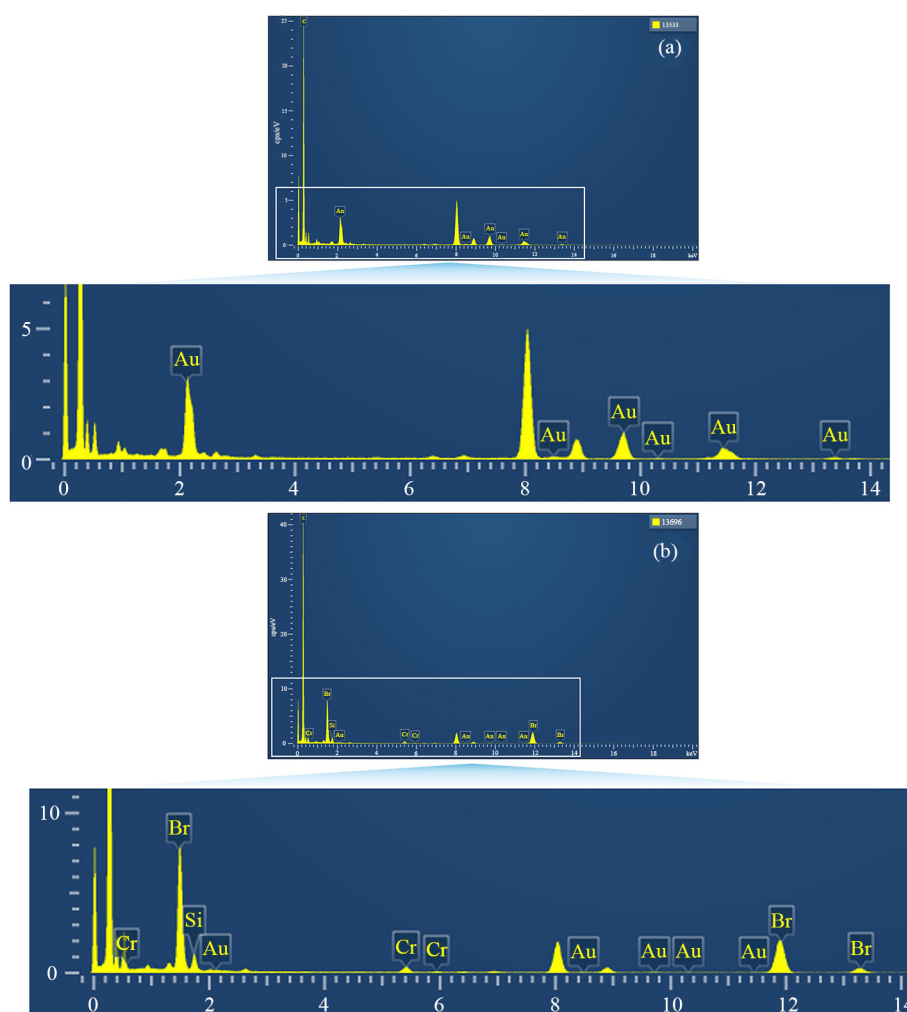


Figure 7. EDS spectra of (a) PUF-AuNPs and (b) after exposing to  $\text{Cr}^{6+}$  in 1 M HBr when x-axis is energy (keV) and y-axis is CPS (eV)



**Table 1.** The results of the EDS analysis

Element	Atom (%)		Weight (%)	
	A*	B**	A*	B**
C	99.3	95.7	90.0	87.3
O	-	2.1	-	2.5
Si	-	0.6	-	1.4
Au	0.7	-	10.0	-
Cr	-	0.4	-	1.5
Br	-	1.2	-	7.3
Total	100.0	100.0	100.0	100.0

\* A was PUF-AuNPs (n = 2)

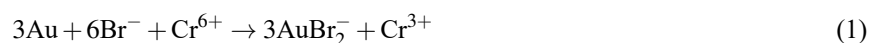
\*\* B was PUF-AuNPs after exposing to Cr<sup>6+</sup> in 1 M HBr (n = 4)

## 5. The mechanisms for detection of Cr<sup>6+</sup> using PUF-AuNPs

AuNPs sorbed on PUF would be unstable in an acidic medium like HBr due to covering by Br<sup>-</sup>. AuNPs were easily dissolved into the solution. Expected two different mechanisms were attained when PUF-AuNPs were placed on 0.05 and 1 M HBr.

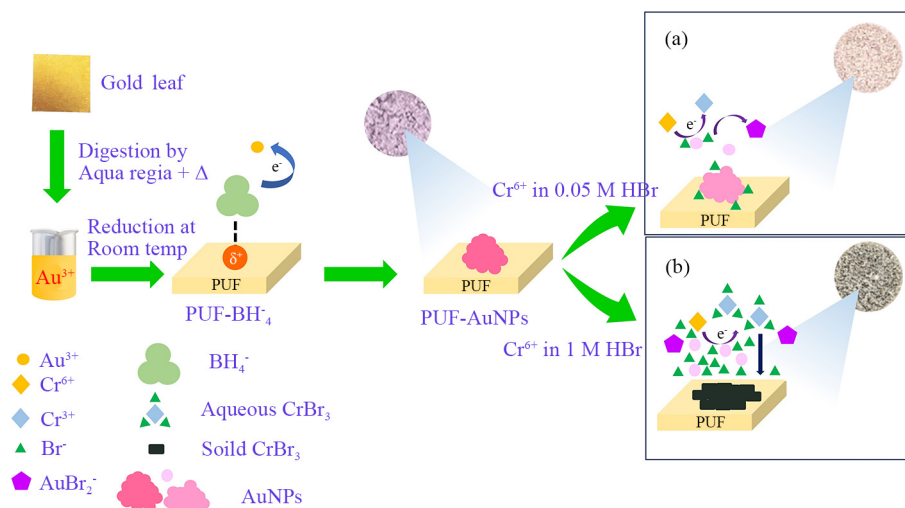
### 5.1 Leaching of AuNPs

The electrostatic potential of this process could be discussed. Generally, Au<sup>0</sup> cannot be oxidized to Au<sup>+</sup> by Cr<sup>6+</sup> due to its higher reduction potential. The leaching of AuNPs from the surface of PUF occurred when PUF-AuNPs were presented in 0.05 M HBr solution (Figure 8a). In this condition, the reduction potential of Au<sup>+</sup>/Au<sup>0</sup> would decrease because of the forming of AuBr<sub>2</sub><sup>-</sup> complexes which Br<sup>-</sup> roles as a ligand. The reduction potential of Cr<sup>6+</sup>/Cr<sup>3+</sup> increased due to the increment of hydrogen ions. This allowed Cr<sup>6+</sup> to oxidize AuNPs (Equation (1))<sup>6,11</sup>. The red-purple color of PUF-AuNPs diminished proportionally to the concentration of Cr<sup>6+</sup>.



### 5.2 Precipitation of CrBr<sub>3</sub>

A precipitate appeared when the PUF-AuNPs were exposed to 1 M HBr solution (Figure 8b), and the increase of precipitate was proportional to the concentration of Cr<sup>6+</sup>. First, Cr<sup>6+</sup> might be reduced to Cr<sup>3+</sup> by AuNPs on the surface of PUF from Equation (1). Next, with excessive Br<sup>-</sup>, the reduced Cr<sup>3+</sup> might form a compound with excess Br<sup>-</sup> as CrBr<sub>3</sub>. The expected process and sediment agreed with EDS, such as the disappearance of Au and the appearance of Cr and Br accorded to SEM and TEM images. From the solid phase stabilizing ability of PUF, the precipitate could form and be stable on its surface. It should be noted that the colorimetric detection of Cr<sup>6+</sup> based on the precipitation on PUF-AuNPs has yet to be reported elsewhere.



**Figure 8.** The expected mechanisms for leaching and precipitation after exposing PUF-AuNPs in (a) 0.05 and (b) 1 M HBr

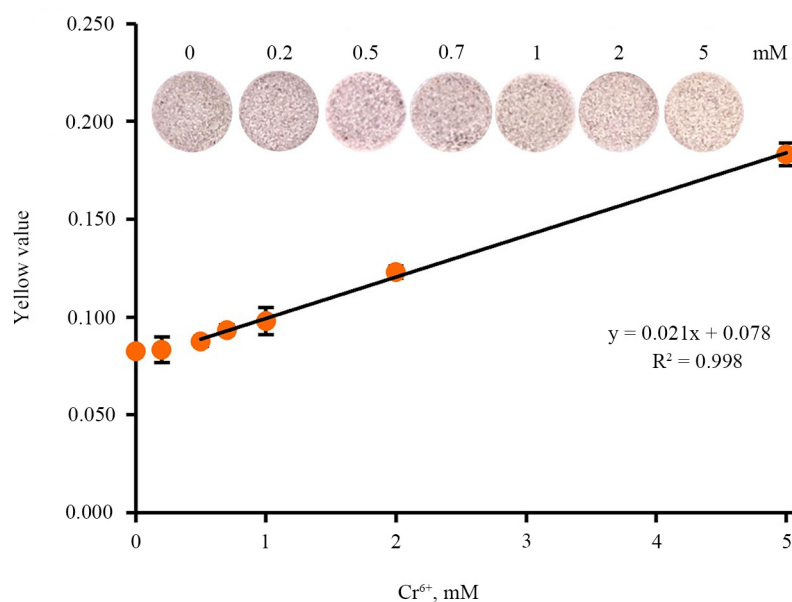
### 5.3 Type of acids

The standard reduction potential of  $\text{Cr}^{6+}$  is 1.33 V, which is lower than  $\text{Au}^+$  at 1.69 V<sup>6,11</sup>. The reduction of  $\text{Cr}^{6+}/\text{Cr}^{3+}$  is unaffordable. To oxidize AuNPs, the detection of  $\text{Cr}^{6+}$  was conducted in an acidic medium such as hydrochloric acid and hydrobromic acid to decrease the reduction potential of  $\text{Au}^0$  to be lower than  $\text{Cr}^{6+}$ . The detection of  $\text{Cr}^{6+}$  in different acids gave a linear relation and related to  $\text{Cr}^{6+}$  concentrations for hydrobromic acid with the linear equation as yellow value =  $0.022[\text{Cr}^{6+}, \text{mM}] + 0.080$  ( $R^2 = 0.996$ ) while using hydrochloric acid was no linear relation: yellow value =  $0.001[\text{Cr}^{6+}, \text{mM}] + 0.094$  ( $R^2 = 0.077$ ). The intensity in the yellow value would increase when the concentration of  $\text{Cr}^{6+}$  in hydrobromic acid increased. The red-purple color of the sorbed AuNPs on PUF leached out due to the oxidation of  $\text{Au}^0$ .

## 6. Analytical characteristics

### 6.1 The presence of $\text{Cr}^{6+}$ in 0.05 M HBr

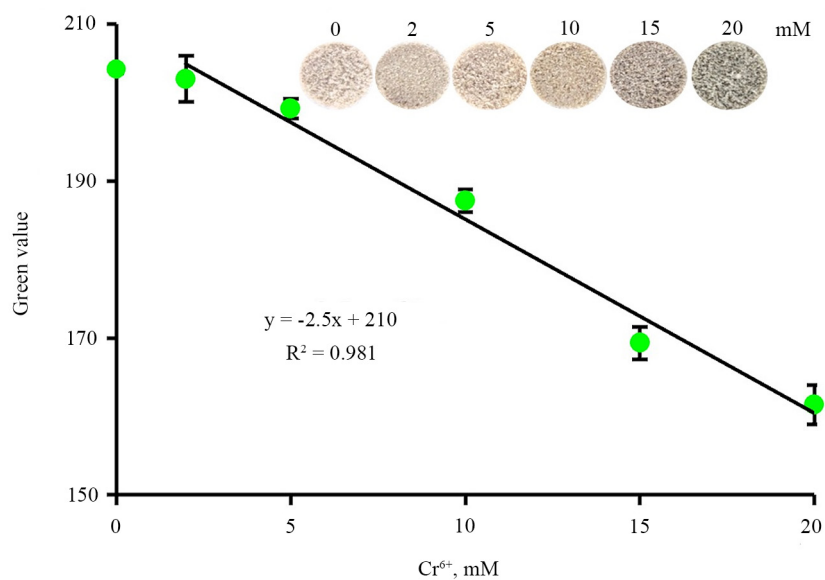
The image characteristics of the smartphone for  $\text{Cr}^{6+}$  in 0.05 M HBr were studied, including red, green, blue, cyan, purple, and yellow, which are the color properties. It was found that the yellow value resulted in a good linear relationship and higher sensitivity than those single-color modes with  $\text{Cr}^{6+}$  concentration. This color value was chosen for detection. Under the optimum condition of the proposed method, the calibration graph (Figure 9) was obtained: yellow value =  $0.021[\text{Cr}^{6+}, \text{mM}] + 0.078$  ( $R^2 = 0.998$ ) for 0.5–5 mM of  $\text{Cr}^{6+}$ . The limit of quantitation (LOQ), was 0.3 mM ( $\text{LOQ} = 10\delta/S$  where  $\delta$  is the standard deviation of the blank measurements and  $S$  is the slope of the calibration graph). The precision was tested at 0.5 mM  $\text{Cr}^{6+}$  and less than 4% RSD ( $n = 9$ ).



**Figure 9.** The linear calibration for detecting Cr<sup>6+</sup> in a low concentration range with yellow value

## 6.2 The presence of Cr<sup>6+</sup> in 1 M HBr

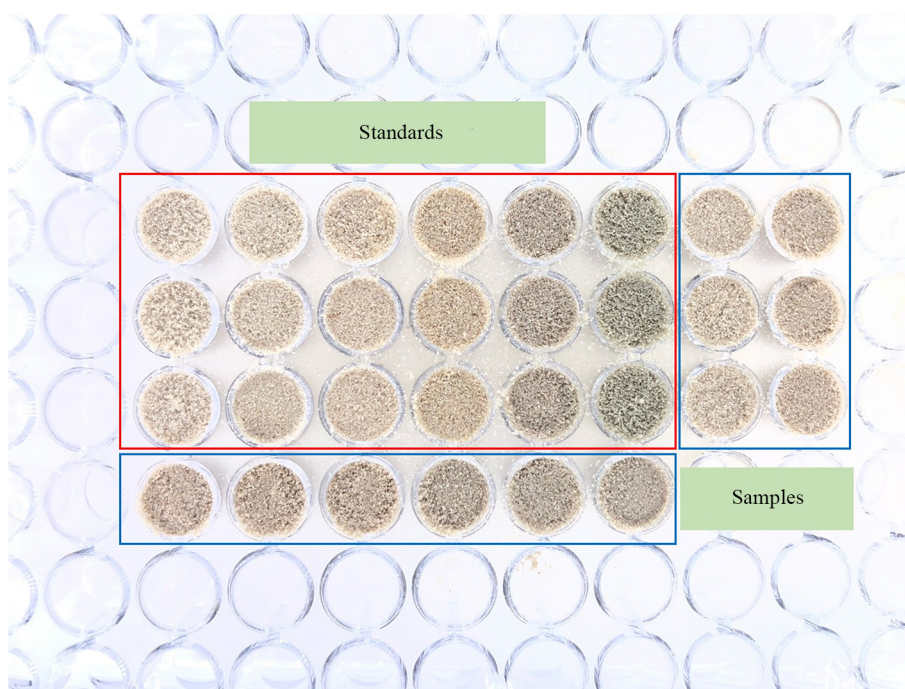
In the same manner, the color mode for the image obtained from the detection of Cr<sup>6+</sup> in 1 M HBr was investigated. It was found that the green value resulted in a linear relationship and higher sensitivity than other single-color channels with Cr<sup>6+</sup> concentration. This color value was chosen for detection. The linear calibration of the assay of Cr<sup>6+</sup> in the presence of 1 M HBr (Figure 10) provided a higher linear range than 0.05 M HBr as 2–20 mM of Cr<sup>6+</sup> with green value =  $-2.5[\text{Cr}^{6+}, \text{mM}] + 210$  ( $R^2 = 0.981$ ) and the limit of detection (LOD) at 0.6 mM (LOD =  $3\delta/S$ ).



**Figure 10.** The linear calibration for the detection of Cr<sup>6+</sup> in a high concentration range with green value

### 6.3 The proposed procedure for Cr<sup>6+</sup> determination

Two proposed procedures for Cr<sup>6+</sup> determination were tested in known samples of aqueous solutions (n = 3). Following the general procedure, the exposed PUF-AuNPs powder was put on the 96 well plates (Figure 11). The available wells were the central 32 wells, which were not affected by the shadow from an adjacent well. For example, the standard solution of Cr<sup>6+</sup> in 1 M HBr with various concentrations: 0, 2, 5, 10, 15, and 20 mM were in the red line box, and 4 known samples were in the blue line boxes with 3 replications. A one-shot image was taken under the light-controlled photograph box. The calibration graph was plotted daily, and the amount of Cr<sup>6+</sup> was calculated for all procedures and observed with the naked eye for the second procedure. The one-shot image would allow the same photo conditions for both standards and samples and reduce time. In Table 2, the results were presented, and the amount of Cr<sup>6+</sup> was found from the known aqueous samples in 0.05 M HBr (No. 1 to 4) and 1 M HBr (No. 5 to 8). The relative error was evaluated to assess the accuracy of the result. The Cr<sup>6+</sup> in samples No. 1 to 4 was  $0.8 \pm 0.1$ – $0.9 \pm 0.1$  mM with a relative error between –31 to 14%, and No. 5 to 8 was  $5 \pm 2$ – $13 \pm 2$  mM with a relative error between –7 to 22%. The naked-eyes detection was applied for the second linear calibration method with a relative error between –17 to 11%.



**Figure 11.** The 32 available wells with the set of PUF-AuNPs after the detection of 6 concentrations of standard Cr<sup>6+</sup> (red box) and 4 known aqueous samples (blue box) with triplicates

**Table 2.** Hexavalent chromium content in samples of known aqueous solutions

Sample	Known Sample	Found	Cr <sup>6+</sup> (mM)		
			Relative Error (%)	Naked-Eyes Detected	Relative Error (%)
1	0.7	$0.8 \pm 0.1$	14	-	-
2	0.9	$0.8 \pm 0.1$	-11	-	-
3	0.9	$0.8 \pm 0.1$	-11	-	-
4	1.3	$0.9 \pm 0.1$	-31	-	-
5	6	$5 \pm 2$	-17	5	-17
6	9	$9 \pm 1$	0	10	11
7	9	$11 \pm 1$	22	10	11
8	14	$13 \pm 2$	-7	15	7

In recent years, using sensors with electrochemical analysis with a minute duration provided high sensitivity for Cr<sup>6+</sup> detection with LOQs of  $7.5 \times 10^{-5}$ – $5.8 \times 10^{-4}$  mM<sup>9,10</sup> which were converted from the reported LODs by calculating  $LOQ = 3.3LOD$ . The colorimetric sensors of functionalized AuNPs solutions with UV-Visible spectrometer reported LOQs of  $6.6 \times 10^{-5}$ – $0.004$  mM<sup>4,6–8</sup> while obtained LOQs from image processing and naked eyes were to be  $5.0 \times 10^{-4}$ – $0.01$  mM with an analysis time between 0.5–25 min<sup>11–15</sup>.

Even though the demonstration of two new different colorimetric detections for the sensing of Cr<sup>6+</sup> using AuNPs sorbed on the solid phase of PUF with a smartphone and one-shot image processing or naked eyes may not be sensitive as those works at this time<sup>4,6–15</sup>, but it offered other advantages, namely, the cost-effectiveness of hydrogen tetrachloroaurate (III) which was obtained from a gold leaf and using a smartphone as a detector. This would be useful for a place where the budget is limited. Simple apparatuses, procedures, and mind conditions for the preparation were included. Due to AuNPs sorbed on PUF, a solid-phase stabilizer, the PUF-AuNPs could be kept at room temperature instead of in a fridge. Regarding analysis time, the proposed procedure required longer than those reports from exposure to the Cr<sup>6+</sup> solution until image processing. One standard calibration with at least four samples in triplicate could be done at the same time from the benefit of a one-shot image. It should be noted that the number of concentrations of the standard Cr<sup>6+</sup> solutions or replications can be reduced to increase the number of samples within 32 wells of the plastic well plate. This would compensate for the time for analysis.

## 7. Conclusions

Two different colorimetric sensings based on leaching and precipitating mechanisms for hexavalent chromium assay using the composite PUF-AuNPs operated with the smartphone and image processing were proposed. Apart from hydrogen tetrachloroaurate (III), it was prepared from a low-cost and locally available gold leaf before being reduced to AuNPs on the PUF surface with mind conditions and could be stored at room temperature. These will be the advantages for tight budget. PUF could be readily synthesized in the lab with simple apparatuses. PUF-AuNPs preparation and detection procedure were successfully confirmed by various techniques such as FT-IR, SEM, TEM, and EDS. The proposed method provided two linear calibrations with two different shades of color for detecting Cr<sup>6+</sup>. The plastic well plate with a one-shot image could provide at least one standard calibration with at least four samples in triplicate to obtain the same photo conditions. Within the 32 wells of the plastic well plate, the number of standard concentrations or replications can be decreased to allow for more samples. This would reduce the time for analysis. The proposed method has been demonstrated by the assay of Cr<sup>6+</sup> in aqueous samples with calculation in a calibration graph and the naked eye.

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## Conflict of Interests

The authors declare no conflict of interest.

## References

- [1] Ye, J.; Wang, Y.; Bai, Y.; Zhang, W.; He, W. A Highly Selective Turn-On Fluorescent Chemodosimeter for Cr(VI) and Its Application in Living Cell Imaging. *RSC Adv.* **2014**, *4*, 2989–2992. <https://doi.org/10.1039/C3RA46543H>.

- [2] Pollution Control Department of Thailand. Water Quality Management in Thailand. Available online: <https://www.pcd.go.th/waters/%E0%B9%80%E0%B8%AD%E0%B8%81%E0%B8%AA%E0%B8%B2%E0%B8%A3-water-quality-management-in-thailand> (accessed on 11 May 2024).
- [3] Czapla, M.; Szopa, S.; Grygoyć, K.; Łyko, A.; Michalski, R. Development and Validation of HPLC–ICP-MS Method for the Determination Inorganic Cr, As and Sb Speciation Forms and Its Application for Pławniowice Reservoir (Poland) Water and Bottom Sediments Variability Study. *Talanta* **2014**, *120*, 475–483. <https://doi.org/10.1016/j.talanta.2013.11.092>.
- [4] Amanulla, B.; Subbu, H. K. R.; Ramaraj, S. K. A Sonochemical Synthesis of Cyclodextrin Functionalized Au-FeNPs for Colorimetric Detection of Cr<sup>6+</sup> in Different Industrial Waste Water. *Ultrason. Sonochem.* **2018**, *42*, 747–753. <https://doi.org/10.1016/j.ultsonch.2017.12.041>.
- [5] Borges, A. R.; François, L. L.; Becker, E. M.; Vale, M. G. R.; Welz, B. Method Development for the Determination of Chromium and Thallium in Fertilizer Samples Using Graphite Furnace Atomic Absorption Spectrometry and Direct Solid Sample Analysis. *Microchem. J.* **2015**, *119*, 169–175. <https://doi.org/10.1016/j.microc.2014.11.007>.
- [6] Guo, J.; Hou, C.; Yang, M.; Huo, D.; Li, J.; Fa, H.; Luo, H.; Yang, P. Colorimetric Sensing of Chromium(VI) Ions in Aqueous Solution Based on the Leaching of Protein-Stabled Gold Nanoparticles. *Anal. Methods* **2016**, *8*, 5526–5532. <https://doi.org/10.1039/C6AY01200K>.
- [7] Li, S.; Wei, T.; Ren, G.; Chai, F.; Wu, H.; Qu, F. Gold Nanoparticles Based Colorimetric Probe for Cr(III) and Cr(VI) Detection. *Colloids Surf. A: Physicochem. Eng. Asp.* **2017**, *535*, 215–224. <https://doi.org/10.1016/j.colsurfa.2017.09.028>.
- [8] Sui, N.; Liu, F.; Li, T.; Wang, L.; Wang, T.; Liu, M.; Yu, W. W. Colorimetric Detection of Ascorbic Acid Based on the Trigger of Gold Nanoparticles Aggregation by Cr(III) Reduced from Cr(VI). *Anal. Sci.* **2017**, *33*, 963–967. <https://doi.org/10.2116/analsci.33.963>.
- [9] Xu, Y.; Xiong, C.; Gao, C.; Li, Y.; Bian, C.; Xia, S. Cathodically Pretreated AuNPs–BDD Electrode for Detection of Hexavalent Chromium. *Micromachines* **2020**, *11*, 1095. <https://doi.org/10.3390/mi11121095>.
- [10] An, Y.; Wang, W.; Lv, Q.; Zhang, Q.; Wang, X. A Dual-Readout Paper-Based Analytical Device for the Simultaneous Determination of Hexavalent Cr and Total Cr. *Mikrochim. Acta* **2022**, *189*, 445. <https://doi.org/10.1007/s00604-022-05532-x>.
- [11] Guo, J.; Huo, D.; Yang, M.; Hou, C.; Li, J.; Fa, H.; Luo, H.; Yang, P. Colorimetric Detection of Cr(VI) Based on the Leaching of Gold Nanoparticles Using a Paper-Based Sensor. *Talanta* **2016**, *161*, 819–825. <https://doi.org/10.1016/j.talanta.2016.09.032>.
- [12] Liu, S.; Wang, X.; Zou, C.; Zhou, J.; Yang, M.; Zhang, S.; Huo, D.; Hou, C. Colorimetric Detection of Cr<sup>6+</sup> Ions Based on Surface Plasma Resonance Using the Catalytic Etching of Gold Nano-Double Cone @ Silver Nanorods. *Anal. Chim. Acta* **2021**, *1149*, 238141. <https://doi.org/10.1016/j.aca.2020.12.016>.
- [13] Qi, Y.; Li, B.; Song, D.; Xiu, F.; Gao, X. Ultrafast Colorimetric Detection of Cr(VI) Based on Competition of 8-HQ to Cr(VI) and TMB Oxides Using GO/AuNPs Nanocomposites as Peroxidase Mimic. *Spectrochim. Acta, Part A* **2023**, *297*, 122722. <https://doi.org/10.1016/j.saa.2023.122722>.
- [14] Dong, C.; Wu, G.; Wang, Z.; Ren, W.; Zhang, Y.; Shen, Z.; Li, T.; Wu, A. Selective Colorimetric Detection of Cr(III) and Cr(VI) Using Gallic Acid Capped Gold Nanoparticles. *Dalton Trans.* **2016**, *45*, 8347–8354. <https://doi.org/10.1039/C5DT04099J>.
- [15] Wei, J.; Yang, L.; Yue, G.; Zhu, J.; Huang, D.; Zhao, P. Nitrotriacetate-Stabilized Gold Nanoparticles: A Novel Strategy for the Colorimetric Detection of Cr(III)/Cr(VI) and the Mechanistic Aspects. *Anal. Methods* **2017**, *9*, 2805–2811. <https://doi.org/10.1039/C7AY00989E>.
- [16] Mohamed, A.; Li, X.; Li, C.; Li, X.; Yuan, C.; Barakat, H. Smartphone-Based Colorimetric Detection of Chromium (VI) by Maleic Acid-Functionalized Gold Nanoparticles. *Appl. Sci.* **2021**, *11*, 10894. <https://doi.org/10.3390/app112210894>.
- [17] Muthwa, S. F.; Makhanya, T. R.; Mlambo, M.; Shumbula, N. P.; Shumbula, P. M.; Onwubu, S. C.; Moloto, N.; Gengan, R. M.; Mdluli, P. S. Synthesis and Characterization of 3-(p-Tolyl)-2,3-Dihydropyrazolo[3,4-b]Indole-1(4H)-Carbothioamide Functionalized Gold Nanoparticles for the CIEL\*a\*b\*/Yxy Colorimetric Detection of Cr(VI). *J. Mol. Struct.* **2020**, *1209*, 127985. <https://doi.org/10.1016/j.molstruc.2020.127985>.
- [18] Kulandaivel, S.; Lo, W.; Lin, C.; Yeh, Y. Cu-PyC MOF with Oxidoreductase-Like Catalytic Activity Boosting Colorimetric Detection of Cr(VI) on Paper. *Anal. Chim. Acta* **2022**, *1227*, 340335. <https://doi.org/10.1016/j.aca.2022.340335>.

- [19] Isachenko, A. I.; Melekhin, A. O.; Apyari, V. V.; Volkov, P. A.; Dmitrienko, S. G. Determination of Melamine by Diffuse Reflectance Spectroscopy by Its Effect on the Formation of a Gold–Polyurethane Foam Nanocomposite. *J. Anal. Chem.* **2021**, *76*, 315–321. <https://doi.org/10.1134/S1061934821030060>.
- [20] Melekhin, A. O.; Isachenko, A. I.; Apyari, V. V.; Volkov, P. A.; Dmitrienko, S. G.; Torocheshnikova, I. I.; Zolotov, Y. A. Effect of Amines on Formation of Gold/Polyurethane Foam Nanocomposites and Its Sensing Opportunities. *Talanta* **2021**, *226*, 122151. <https://doi.org/10.1016/j.talanta.2021.122151>.
- [21] Phongphut, A.; Chayasombat, B.; Cass, A. E. G.; Sirisuk, A.; Phisalaphong, M.; Prichanont, S.; Thanachayanont, C. Clay/Au Nanoparticle Composites as Acetylcholinesterase Carriers and Modified-Electrode Materials: A Comparative Study. *Appl. Clay Sci.* **2020**, *94*, 105704. <https://doi.org/10.1016/j.clay.2020.105704>.
- [22] Issarangkura Na Ayutthaya, P.; Yeerum, C.; Kesonkan, K.; Kiwfo, K.; Grudpan, K.; Teshima, N.; Murakami, H.; Vongboot, M. Lead Assays with Smartphone Detection Using a Monolithic Rod with 4-(2-Pyridylazo) Resorcinol. *Molecules* **2021**, *26*, 5720. <https://doi.org/10.3390/molecules26185720>.
- [23] Issarangkura Na Ayutthaya, P.; Vongboot, M. Micro-Milli Scale for the Removal of Iron and Copper by a Positively Charged Foam Before Nickel Colorimetric Detection Using Handy Spectrometer. *Curr. Top. Chem.* **2024**, *4*, 1–7. <https://doi.org/10.2174/0126660016300603240528050146>.
- [24] Kimling, J.; Maier, M.; Okenve, B.; Kotaidis, V.; Ballot, H.; Plech, A. Turkevich Method for Gold Nanoparticle Synthesis Revisited. *J. Phys. Chem. B* **2006**, *110*, 15700–15707. <https://doi.org/10.1021/jp061667w>.
- [25] Huang, X.; El-Sayed, M. A. Gold Nanoparticles: Optical Properties and Implementations in Cancer Diagnosis and Photothermal Therapy. *J. Adv. Res.* **2010**, *1*, 13–28. <https://doi.org/10.1016/j.jare.2010.02.002>.
- [26] Zhao, C.; Zhong, G.; Kim, D.; Liu, J.; Liu, X. A Portable Lab-on-a-Chip System for Gold-Nanoparticle-Based Colorimetric Detection of Metal Ions in Water. *Biomicrofluidics* **2014**, *8*, 052107. <https://doi.org/10.1063/1.4894244>.
- [27] Subara, D.; Jaswir, I. Gold Nanoparticles: Synthesis and Application for Halal Authentication in Meat and Meat Products. *Int. J. Adv. Sci. Eng. Inf. Technol.* **2018**, *8*, 1633–1641. <https://doi.org/10.18517/IJASEIT.8.4-2.7055>.
- [28] HQ Graphene. CrBr<sub>3</sub> (Chromium Bromide). Available online: <https://www.hqgraphene.com/CrBr3.php> (accessed on 11 May 2024).