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## ARTICLE

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## Electrochemical fabrication of gold nanoparticles decorated on activated fullerene C60; An enhanced sensing platform for trace level detection of toxic hydrazine in water samples

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A novel and highly sensitive amperometric hydrazine sensor was fabricated using gold nanoparticles (AuNPs) decorated on activated fullerene C60 (AC60) modified screen printed carbon electrode (SPCE). Electrochemical method was used for the fabrication of AC60-AuNPs modified SPCE and characterized by scanning electron microscopy and elemental analysis. The fabricated AC60-AuNPs modified SPCE showed enhanced electrocatalytic activity towards hydrazine than that of other modified SPCEs. Furthermore, the detection potential of hydrazine was quite lower (0.161 V) at AuNPs decorated AC60 modified SPCE than AuNPs decorated bare (0.208 V) and C60 (0.186 V) modified SPCEs. Under optimum conditions, the amperometric response of the sensor was linear over the hydrazine concentrations from 0.13  $\mu$ M to 1.21 mM with a fast response time of 1.3 s. In addition, the proposed sensor showed the lowest limit of detection (LOD) of 0.038  $\mu$ M with a high sensitivity of 0.583  $\mu$ A  $\mu$ M<sup>-</sup>  $^{1}$  cm<sup>-2</sup>. The sensor also holds its high selectivity in the presence of common metal ions and biologically active interfering species. In addition, the practicality of the fabricated sensor in tap water samples are HPLC method. comparable with those detected by

#### 1. Introduction

Hydrazine is one of well-known toxic environmental pollutant, and it can easily damage the kidneys, livers, lungs and nervous system of the human.<sup>1</sup> According to the Environmental Protection Agency (EPA), the exposure of hydrazine in human can result to pneumonia, lung damage, throat irritation, temporary blindness and dizziness.<sup>2</sup> In addition, the severe exposure hydrazine can result into the death.<sup>3</sup> Hydrazine is widely used in different potential applications, such as nickel plating, fuel cells, rocket propulsion systems, removal of halogens from wastewaters, corrosion inhibitor, photograph development, boiler water treatment, blowing agent for producing plastics, production of agricultural chemicals and reducing agent in nuclear fuel reprocessing.<sup>4-6</sup> Therefore, the trace level detection of hydrazine in real samples is more important and highly encouraged. Till date, different methods have been used for the sensitive detection of hydrazine, including spectrophotometry, electrochemical chromatography, chemiluminescence and methods.<sup>7-11</sup> However, the electrochemical methods are widely used

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for detection of hydrazine owing to its high sensitivity, fast response and simplicity.<sup>12</sup> It is well known that hydrazine is electrochemically active in conventional electrodes such as, glassy carbon electrode, screen printed carbon and graphite electrodes.<sup>13</sup> However, the electrochemical oxidation of hydrazine is appeared in conventional electrodes at quite high overpotential with low sensitivity, which resulting to the poor selectivity and reproducibility.<sup>13</sup>

The metal nanoparticles and metal oxides such as Au, Pd, Co, Ag, Pt and ZnO have been widely used for the detection of hydrazine due to their size depended electrochemical properties.<sup>14-19</sup> Among different nanomaterials, gold nanoparticles (AuNPs) are of particular interest as an electrocatalyst for the oxidation of hydrazine due to its high electrocatalytic activity, a high surface-to-volume ratio and low overpotential.<sup>20, 21</sup> Recently, the composites of AuNPs with carbon nanotubes, graphene, activated carbon and graphite have also been used for the detection of hydrazine. The AuNPs modified carbon nanomaterials showed an enhanced sensitivity, stability along with low limit of detection and overpotential than that of AuNPs modified electrodes.<sup>22-26</sup> However, trace level detection of hydrazine at low overpotential using novel composites has always received much attention in the scientific community. On the other hand, fullerene C60 (C60) is one of the carbon allotrope and has been used as a promising electron transfer mediator for different disciplines including electrocatalysis.<sup>27, 28</sup> The electrochemical activity of C60 is poor in aqueous solutions, hence the electrochemical activation of C60 is mandatory for the use in aqueous solutions. In addition, the electrochemically activated C60 (AC60) showed enhanced electron transfer ability towards the electrode surface and resulting to the electrocatalysis of different small molecules.<sup>29, 30</sup> Till date, only few reports have been reported for the fabrication of metal nanoparticles decorated C60 or AC60 for electrochemical applications.<sup>31, 32</sup> Recently, we have fabricated AC60-PdNPs composite for enhanced

electrochemical sensing of dopamine. Furthermore, the unique properties of AC60 is a suitable candidate for fabrication of AC60metal nanoparticles composites and construction of robust electrochemical sensors.<sup>31</sup> To the best of our knowledge, for the first time we report the electrochemical fabrication of AuNPs decorated AC60 composite and application for trace level detection of hydrazine.

In the present work, we report the electrochemical fabrication of AuNPs decorated AC60 modified SPCE for amperometric detection of hydrazine. A simple electrochemical method was used for the fabrication of AC60-AuNPs modified SPCE. The optimization of AuNPs electrodeposition on AC60 towards the response to hydrazine was studied and discussed in detail. An enhanced electrocatalytic response with lower overpotential of hydrazine was observed at AC60-AuNPs modified SPCE than that of other modified SPCEs. The selectivity and practicality of the sensor has also been critically studied and discussed in detail.

#### 2. Experimental

#### Materials and methods

Fullerene-C60 (99.5% purity) was obtained from Sigma–Aldrich. Screen printed carbon electrode was purchased from Zensor R&D Co., Ltd., Taipei, Taiwan. Potassium gold (III) chloride trihydrate (K(AuCl<sub>4</sub>.3H<sub>2</sub>O) was purchased from Strem chemicals (USA). Hydrazine was obtained from Sigma–Aldrich and used as received. Ascorbic acid, uric acid and dopamine were obtained from Sigma– Aldrich. The supporting electrolyte pH 7 (PBS) was prepared by using 0.05 M Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> solutions and other pH solutions were adjusted using 0.5 M H<sub>2</sub>SO<sub>4</sub> and 2 M NaOH. All other chemicals used were of analytical grade and the solutions were prepared with the help of Millipore water.

Electrochemical measurements including amperometric method were performed using CHI 1205B electrochemical analyzer. Surface

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morphological studies were carried out using Hitachi S-3000 H scanning electron microscope (SEM). Elemental analysis (EDX) was studied using HORIBA EMAX X-ACT energy-dispersive X-ray spectrometer that was attached to Hitachi S-3000 H scanning electron microscope. Electrochemical impedance spectroscopy (EIS) studies were performed using IM6ex ZAHNER (Kroanch, Germany). The AC60-AuNPs modified SPCE with an active surface area of 0.184 cm<sup>2</sup> was used as a working electrode; Ag/AgCl electrode (Sat. KCl) and a platinum wire was used as a reference and counter electrodes, respectively.

#### Electrochemical preparation of AC60-AuNPs modified SPCE

The AC60 modified SPCE was prepared by according to our previous reported method [31]. Briefly, about 8  $\mu$ L of C60 toluene dispersion (0.5 mg/mL) was drop coated on SPCE and dried at a room temperature. The C60 modified SPCE was further electrochemically activated in 1 M KOH solution in the potential scanning between 0 to 1.5 V for 3 cycles at a scan rate of 10 mV s<sup>-1</sup>, as reported elsewhere.<sup>30</sup>



Scheme 1 Schematic representation for the fabrication of AC60-AuNPs modified SPCE and oxidation of hydrazine.

The fabricated AC60 modified SPCE was transferred into the electrochemical cell containing 1.3 mM K(AuCl<sub>4</sub>).3H<sub>2</sub>O with 0.5 M  $H_2SO_4$  solution. The AuNPs were electrodeposited on AC60 modified SPCE after the 5 successive CV cycles in the potential range between -0.2 to 1.5 V at a scan rate of 50 mVs<sup>-1</sup>. The resulting AC60-AuNPs modified SPCE was dried at room temperature and used for the detection of hydrazine. The schematic representation for

the fabrication of AC60-AuNPs modified SPCE and its electrochemical oxidation of hydrazine is shown in Scheme. 1.

The electrodeposition of AuNPs on AC60 (red profile) and C60 (blue profile) modified SPCEs are shown in Fig. 1. Fig. 1 shows the electrochemical deposition of AuNPs on AC60 (red line) and C60 (blue line) modified SPCEs after 5 consecutive cyclic voltammograms in the electrochemical cell containing 1.3 mM K(AuCl<sub>4</sub>).  $3H_2O + 0.5 \text{ M H}_2SO_4$  at the scan rate of 50 mV s<sup>-1</sup>. The full cyclic voltammograms for the electrodeposition of AuNPs on C60 and AC60 are shown in Fig. S1. It can be seen from Fig. 1 and S1 that the formation of Au oxides is observed at the potential of 1.16 V and it is subsequently reduced to metallic AuNPs at the potential of 0.77 V on the reverse scan.<sup>33</sup> The similar phenomenon has been reported elsewhere for the electrodeposition of AuNPs on carbon modified electrodes.<sup>25, 33, 34</sup> In addition, the CV profile of electrodeposition of AuNPs on AC60 and C60 is much similar, which indicates that the formation of AuNPs was not affected by surface nature of modified SPCE.



Fig. 1 Electrochemical deposition of AuNPs on AC60 (red line) and C60 (blue line) modified SPCEs after 5 consecutive cyclic

voltammograms in the electrochemical cell containing 1.3 mM  $K(AuCl_4)$ .  $3H_2O + 0.5 M H_2SO_4$  at the scan rate of 50 mV s<sup>-1</sup>.

However, the enhanced CV profile of AC60 modified SPCE clearly indicates that the electrodeposition of AuNPs is more favourable on AC60 modified SPCE than that of C60 modified SPCE. For compassion, AuNPs decorated on bare and C60 modified SPCEs were prepared by the same method as mentioned above without C60 and AC60. All electrochemical measurements were carried out in an inert atmosphere ( $N_2$  atmosphere) at room temperature.

### 3. Results and Discussion

#### Characterizations

The surface morphology of the different modified electrodes were – characterized by using SEM. Fig. 2 shows SEM images of the (A) – AC60/SPCE, (B) AuNPs/SPCE and AC60-AuNPs/SPCE at higher – (C) and lower magnification (D). It can be seen that the AC60 – reveals its typical rod-shape morphology of C60 and resemble to our – previous report.<sup>31</sup>



Fig. 2 The SEM images of (A) AC60/SPCE, (B) AuNPs/SPCE and AC60-AuNPs/SPCE at higher (C) and lower magnification (D). Scale bar =  $3 \mu m$ .

The SEM of AC60-AuNPs modified SPCE shows that the AuNPs were uniformly decorated on the AC60 surface; and average particle size of AuNPs was found as  $75 \pm 8$  nm on AC60 (Fig. 3D).

Moreover, the size of the AuNPs on AC60 is similar to the size of AuNPs on SPCE (Fig. 3B). The result confirms that the surface of AuNPs were unchanged after the electrochemical activation of C60. The presence of AuNPs on AC60 was further confirmed by EDX and the quantitative results of EDX of AC60-AuNPs modified SPCE and shown in Fig. S2. It can be seen that the metallic Au and C were clearly seen, which is due to the presence of AuNPs and AC60. The findings are confirmed the formation of AuNPs on AC60 modified SPCE.

 Table 1 Comparison of electrochemical parameters of different modified SPCEs.

SPCE	R <sub>s</sub>	R <sub>et</sub>	C <sub>dl</sub>	W
	$(\Omega)$	$(\Omega)$	(µF)	$(\Omega^{-1} s^{0.5})$
bare	30.5	212	314.6	3.8
C60	30.3	192	36.4	4.2
C60-AuNPs	30.5	108	9.2	4.9
AC60/AuNPs	30.5	92	4.3	3.1
$R_S$ – Solution	resistance;	$R_{et}$ –	Electron transfer	r resistance;

 $C_{dl}$  – Double layer capacitance; W – Warburg impedance.

The electrochemical properties of different modified SPCEs were evaluated by EIS, since it is an effective method for evaluating the interfacial and electrochemical properties of modified electrodes.<sup>35</sup> Fig. 3A shows the EIS of bare (a), C60 (b), C60-AuNPs (c) and AC60-AuNPs (d) modified SPCEs in PBS containing 5 mM Fe(CN)6<sup>3-/4-</sup> with 0.1 M KCl. The Randles equivalent circuit model was used for fitting the EIS data and the equivalent circuit model was shown in Fig. 3A inset. The obtained electrochemical parameters (solution resistance (R<sub>s</sub>), electron transfer resistance (R<sub>et</sub>), double layer capacitance (C<sub>dl</sub>), Warburg impedance (W)) of EIS for different modified SPCEs are tabulated in Table 1. It can be seen that the bare and C60 modified SPCEs shows a large semi-circle with an electron transfer resistance (R<sub>et</sub>) of 212 and 192  $\Omega$  than that of C60/AuNPs modified SPCE (108  $\Omega$ ), which indicates

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that bare and C60 modified SPCE has a poor electron transfer towards the electrode surface when compared with C60/AuNPs modified SPCE. While, AC60-AuNPs modified SPCE shows a small semi-circle with a low  $R_{et}$  of 92  $\Omega$ , which indicates that AC60-AuNPs modified SPCE has high electron transferring ability towards electrode surface than that of other modified SPCEs. The unique properties of AuNPs and AC60 are the possible reason for enhanced electron transfer towards the electrode surface. The result confirms that AuNPs decorated AC60 has high electrochemical activity than other modified SPCEs.



Fig. 3 A) EIS of bare (a), C60 (b), C60-AuNPs (c) and AC60-AuNPs (d) modified SPCEs in PBS containing 5 mM  $Fe(CN)6^{3-/4-}$  with 0.1 M KCl; inset shows the Randles equivalent circuit model. B) Cyclic voltammetric response of C60 (a), AC60 (b), C60-AuNPs (c), AuNPs (d), and AC60-AuNPs (e) modified SPCEs for 1 mM hydrazine containing PBS at a scan rate of 50 mV s<sup>-1</sup>.

#### Electrocatalytic oxidation of hydrazine

Before the electrochemical analysis, the optimization of the modified electrode is more important. Hence, we have investigated the effect of different AuNPs electrodeposition cycles with respect to the electrocatalytic activity of 1 mM hydrazine. The results are summarized in Fig. S3A and B. It can be seen that the utmost oxidation current response and lower overpotential of hydrazine was observed for 5 cycles electrodeposited AuNPs on AC60. While, below or more than five cycles of AuNPs deposition on AC60 leads to poor sensitivity and higher overpotential for the detection of hydrazine. Hence, five cycles of AuNPs deposition on AC60 has been used for further electrochemical studies.

The electrocatalytic activity of the different modified electrodes was investigated towards the oxidation of hydrazine in PBS using the CV. Fig. 3B shows the CV response obtained for C60 (a), AC60 (b), C60-AuNPs (c), AuNPs (d) and AC60-AuNPs (e) modified SPCEs for 1 mM hydrazine containing PBS at a scan rate of 50 mV s<sup>-1</sup>. The C60 modified SPCE did not showed apparent oxidation peak response for hydrazine. On the other hand, AC60 modified SPCE shows a weak oxidation peak response at 0.571 V for hydrazine. Under the similar conditions, the AuNPs modified SPCE and C60 exhibits a sharp oxidation peak for hydrazine at the potential of 0.215 and 0.186 V. Moreover, an enhanced peak current response was observed for the oxidation of hydrazine than that of AC60 and C60 modified SPCEs. The result indicates that AuNPs

can greatly enhanced the oxidation of hydrazine and simultaneously reduce the overpotential of hydrazine. However, AC60-AuNPs modified SPCE show a less oxidation overpotential (0.163 V) and enhanced peak current response to hydrazine than that of AuNPs and C60-AuNPs modified SPCEs. The combined unique properties of AC60 and AuNPs are resulting to the enhanced sensitivity and lower overpotential for detection of hydrazine. The result clearly suggests that AC60-AuNPs modified SPCE has high electrocatalytic activity and lower overpotential for the detection of hydrazine than that of other modified SPCEs.



Fig. 4 Cyclic voltammetric response of AC60-AuNPs modified SPCE for 1 mM hydrazine containing PBS at different scan rates from 10 to 120 mV s<sup>-1</sup> (a-e). The corresponding linear plot for  $I_{pa}$  vs. square root of scan rate (inset). Error bar is relative to 3 measurements.

The effect of scan rate on the response to hydrazine was investigated at AC60-AuNPs modified SPCE by CV. Fig. 4A shows the CV response of AC60-AuNPs modified SPCE for 1 mM hydrazine containing PBS at different scan rates from 10 to 120 mV s<sup>-1</sup>. Upon increasing the scan rate, the increase in the oxidation peak current of hydrazine with positive potential shift was observed. As shown in Fig. 4B, the oxidation peak current of hydrazine was linear against the square roots of scan rates from 10 to 120 mV s<sup>-1</sup> with a correlation coefficient of 0.9971, which indicates that the oxidation of hydrazine at AC60-AuNPs modified SPCE is a typical diffusioncontrolled kinetic process. The similar observation has been reported earlier by others using the AuNPs on carbon modified electrodes.<sup>24–</sup> Page 7 of 11

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Fig. 5 A) Cyclic voltammetric response of AC60-AuNPs modified SPCE for 1 mM hydrazine containing different pH solutions (pH 1 to 11) at a scan rate of 50 mV s<sup>-1</sup>. B) Linear dependence of  $I_{pa}$  vs. pH and C)  $E_{pa}$  vs. pH.

The solution pH is greatly affected the electrocatalytic activity of hydrazine, in particular the peak potential of hydrazine. Since, the hydrazine mostly exists in unprotonated form than the protonated form in the solutions.<sup>25</sup> Hence, the pH of the solution is playing an important role on the electro-oxidation of hydrazine. Fig. 5A shows the CV response of AC60-AuNPs modified SPCE for the presence of 1 mM hydrazine in different pH solutions at a scan rate of 50 mV s<sup>-1</sup>. The pH solutions were used pH 1, 3, 5, 7, 9 and 11. The oxidation potential of hydrazine shifts towards the negative direction upon increasing the pH of the solution and shifted towards positive direction upon decreasing the solution pH. In addition, the oxidation peak potential of hydrazine had a linear dependence over the pH ranges from 1 to 11 with a slope value of -80.0 mV/pH (Fig. 5B). The obtained slope value is close to the previously reported literatures slope value for four electrons (e<sup>-</sup>) transferred reaction of electrochemical oxidation of hydrazine.<sup>24–26</sup> The electrochemical oxidation pathway of hydrazine on metal nanoparticles and carbon materials is well studied; therefore, the electro-oxidation of hydrazine via four-electron process and leads to the final product as nitrogen according to the following reaction as reported early.<sup>24–26</sup>

#### $N_2H_4 + 4H_2O \Rightarrow N_2 + 4H_3O^+ + 4e^-$

In addition, the utmost oxidation peak current response of hydrazine was observed at pH 7 solution and the peak current response was decreased when the pH of the solution was more or less than 7 (Fig. 5C). It should be noted that the oxidation peak current of hydrazine was gradually increasing with the pH from 1 to 7 and deceasing with the pH from 7 to 11. At low pH, the protonated form of hydrazine was strongly repelled by the polarized electrode surface, thus leads to the higher overpotential and low oxidation current response. On the other hand, the oxidation peak current response was decrease when the pH of the solution was more than 7.0, which is possibly due to the deprotonation of hydrazine. The higher oxidation peak current response of hydrazine at pH 7 is due to the p $K_a$  of hydrazine is very close to pH 7, since the p $K_a$  of hydrazine is 7.9. The similar observation has been reported earlier for the electrochemical oxidation of hydrazine in different pH solutions. Hence, the pH 7 was used for the electrochemical determination of hydrazine using AC60-AuNPs modified SPCE.

#### Amperometric determination of hydrazine

Amperometric *i-t* method was used for the determination of hydrazine using AC60-AuNPs modified SPCE; since amperometric method is more sensitive, low background current, with high precision method than other voltammetric methods.<sup>25</sup>



**Fig. 6** A) Amperometric *i*–*t* response obtained at AC60-AuNPs modified SPCE for the successive additions of different concentration of hydrazine into the continuously stirred N<sub>2</sub> saturated PBS; Working potential: 0.165 V. Inset of Fig. 5A shows the enlarged view of the amperometric *i*–*t* response for the addition of hydrazine from 0.13  $\mu$ M to 30.13  $\mu$ M. B) The calibration plot of response current vs. [hydrazine].

Fig. 6A shows the amperometric response of AC60-AuNPs modified SPCE for different concentration addition of hydrazine in

constantly stirred N<sub>2</sub> saturated PBS. The working potential was held at 0.161 V. It can be seen that a sharp amperometric response is obtained for the addition of 0.13 µM hydrazine (Fig. 6A inset), which indicates that the rapid electro-oxidation of hydrazine at AC60-AuNPs modified SPCE. The unique combined properties of AuNPs and AC60 which resulting into the fast diffusion of hydrazine on electrode surface. The response time of the sensor was estimated as 1.3 s, which indicates the fast diffusion of hydrazine on AC60-AuNPs modified SPCE. In addition, the AC60-AuNPs modified SPCE exists a stable amperometric response for the further addition of higher concentrations of hydrazine into the solution and amperometric response current was linear over the the concentrations ranging from 0.13 to 1571 µM with the correlation coefficients of 0.9979 (Fig. 6B). The sensitivity was calculated from the fitted equation as 0.557  $\mu A \mu M^{-1}$  cm<sup>-2</sup>. The limit of detection (LOD) was estimated using the standard formula (3 \* Sd of the blank response / slope of the calibration plot) as 0.043  $\mu$ M, where the Sd is  $0.0014 \ \mu A$  and slope value is 0.1074. It is necessary to compare the analytical performance of the developed sensor with the current state of the art, hence the applied potential, LOD, sensitivity and linear response range of the sensor was compared with previously reported AuNPs based hydrazine sensors. The comparative results of the fabricated sensor with other AuNPs based hydrazine sensors are shown in Table. ST1. It can be clearly seen from the Table. ST1, the fabricated AC60-AuNPs modified SPCE exhibits better analytical performance (more than one category) than that of previously reported AuNPs based hydrazine sensors.<sup>1, 14, 20, 24, 25, 37-41</sup> The good analytical performance of sensor is attributed to the combined electrocatalytic activity of AuNPs and AC60, which is resulting to the lower overpotential and enhanced sensitivity for the detection of hydrazine.

Selectivity, practicality and stability of the sensor

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The selectivity of the modified electrode is more important especially in positive working potentials; since, the ascorbic acid (AA), dopamine (DA) and uric acid (UA) are highly active in positive overpotential.



Fig. 7 A) Amperometric i–t response of AC60-AuNPs modified SPCE for the addition of 1.3  $\mu$ M hydrazine (a) and 1000  $\mu$ M of Mg<sup>2+</sup> (b), Ca<sup>2+</sup> (c), Ba<sup>2+</sup> (d) and 200  $\mu$ M of DA (e), AA (f) and UA (g). B) Amperometric i–t response of AC60-AuNPs modified SPCE for the addition of 100  $\mu$ M hydrazine (a) into constantly stirred PBS and its response up to 2000 s. All the experimental conditions are same as in Fig. 6A.

Hence, we evaluate the selectivity of the modified electrode in the presence AA, DA and UA; in addition, we have also used common metal ions for the selectivity studies. The experimental conditions are similar as in Fig. 6A. Fig. 7A shows the amperometric response of AC60-AuNPs modified SPCE for the addition of 1.3  $\mu$ M hydrazine (a) and 1000  $\mu$ M of Mg<sup>2+</sup> (b), Ca<sup>2+</sup> (c), Ba<sup>2+</sup> (d) and 200  $\mu$ M of DA (e), AA (f) and UA (g). A sharp amperometric response is observed for the addition of 1.3  $\mu$ M hydrazine, while common metal ions, DA and UA do not show any response at the modified electrode. However, AA shows a little response at the modified electrode, since AA is known to interfere with the electrochemical detection of hydrazine. Nevertheless, the stable response for hydrazine was observed after the addition of AA. The result indicates that the appropriate selectivity of the fabricated AC60-AuNPs modified SPCE for the detection of hydrazine.

 Table 2 Determination of hydrazine in tap water samples using

 AC60–AuNPs modified SPCE by amperometry.

Sample	Spiked (µM)	Found* (µM)	Found** (µM)	Accuracy (%)
Tap water	1.3	1.322	1.24	93.7
	2.6	2.612	2.57	98.3
	3.9	3.952	3.81	96.4

Detected by Waters Alliance, model 2695 HPLC (Empower, version\_3).

Detected by AC60-AuNPs modified electrode (n=3).

The practical ability of the sensor was evaluated in hydrazine spiked tap water samples from the laboratory using amperometric method. The recovery values were calculated using the standard addition method. In addition, the hydrazine was also detected by traditional HPLC analysis. The detected values of hydrazine by HPLC and electrochemical methods were tabulated in Table. 2. The results obtained using the hydrazine sensor are compared with those obtained using the HPLC method and corresponding calibration plot is displayed in Fig. S4. It can be seen that the results are linear correspond with each other and the electrochemical sensors showed good accuracy (96.1 %) to the results obtained by HPLC method for detection of hydrazine (Table 2). The result clearly validates that the proposed AC60-AuNPs modified electrode can be used for real-time sensing of hydrazine. The operational stability of the modified electrode was examined up to 2000 s by amperometric method and the experimental conditions are similar as of Fig. 6A. The sensor retains its 91.7% of its initial current response after the continuous

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run up to 2000 s in 100  $\mu$ M hydrazine containing constantly stirred PBS (Fig. 7B). The result indicates the excellent operational stability of AC60-AuNPs modified SPCE. The reproducibility and repeatability of the fabricated electrode was evaluated for the detection of 1 mM hydrazine by CV. The reproducibility of 3 electrodes was found with the RSD of 4.1% and repeatability for single sensor for 1 mM hydrazine containing 8 successive PBS measurements was with the RSD of 4.8%.

#### Conclusions

In conclusion, the AuNPs decorated AC60 modified SPCE was fabricated by electrochemical method and used for the sensitive amperometric detection of hydrazine. The SEM reveals that AuNPs were uniformly decorated on AC60 surface with an average size of  $75 \pm 8$  nm. Compared with AuNPs decorated bare and C60 modified SPCEs, the AC60-AuNPs modified SPCE showed an excellent electrocatalytic activity and low oxidation potential for the detection of hydrazine. The fabricated modified electrode shows a wider linear response range, lower LOD, fast response time and high sensitivity for the detection of hydrazine. The good practicality and selectivity of the AC60-AuNPs modified SPCE further authenticates that it can be applied for the practical applications.

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