



# Determination of cyanide in wastewaters using modified glassy carbon electrode with immobilized silver hexacyanoferrate nanoparticles on multiwall carbon nanotube

Meissam Noroozifar<sup>a,\*</sup>, Mozghan Khorasani-Motlagh<sup>b</sup>, Aboozar Taheri<sup>a</sup>

<sup>a</sup> Analytical Research Laboratory, Department of Chemistry, University of Sistan & Baluchestan, Zahedan, P.O. Box 98155-147, Iran

<sup>b</sup> Inorganic Research Laboratory, Department of Chemistry, University of Sistan & Baluchestan, Zahedan, Iran

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## ABSTRACT

The sensitive determination of cyanide in wastewaters using modified GC electrode with silver hexacyanoferrate nanoparticles (SHFNPs) immobilized on multiwall carbon nanotube (MWCNT) was reported. The immobilization of SHFNPs on MWCNT was confirmed by transmission electron microscopy (TEM). The TEM image showed that the SHFNPs retained the spherical morphology after immobilized on MWCNT. The size of SHFNPs was examined around 27 nm. The GC/MWCNT-SHFNPs was used for the determination of cyanide in borax buffer (BB) solution (pH 8.0). Using square wave voltammetry, the current response of cyanide increases linearly while increasing its concentration from 40.0 nM to 150.0 μM and a detection limit was found to be 8.3 nM ( $S/N = 3$ ). The present modified electrode was also successfully used for the determination of 5.0 μM cyanide in the presence of common contaminants at levels presenting in industrial wastewaters. The practical application of the present modified electrode was demonstrated by measuring the concentration of cyanide in industrial wastewater samples. Moreover, the studied sensor exhibited high sensitivity, good reproducibility and long-term stability.

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## 1. Introduction

Monitoring of cyanide in industrial wastes is highly demanded for environmental control, especially in electroplating, precious metal refining and metal cleaning industries [1]. Cyanide is an extremely toxic ion readily absorbed by living organisms by the inhalation, oral and dermal routes of exposure. Lethal levels of cyanide in blood are assumed to be 11.5 mM [2]. In the case of free cyanide, a concentration of 0.77 μM has been reported to be lethal for certain species of sea animals, whereas a concentration of 7.7 μM is allowable for drinking water supplies [2–4].

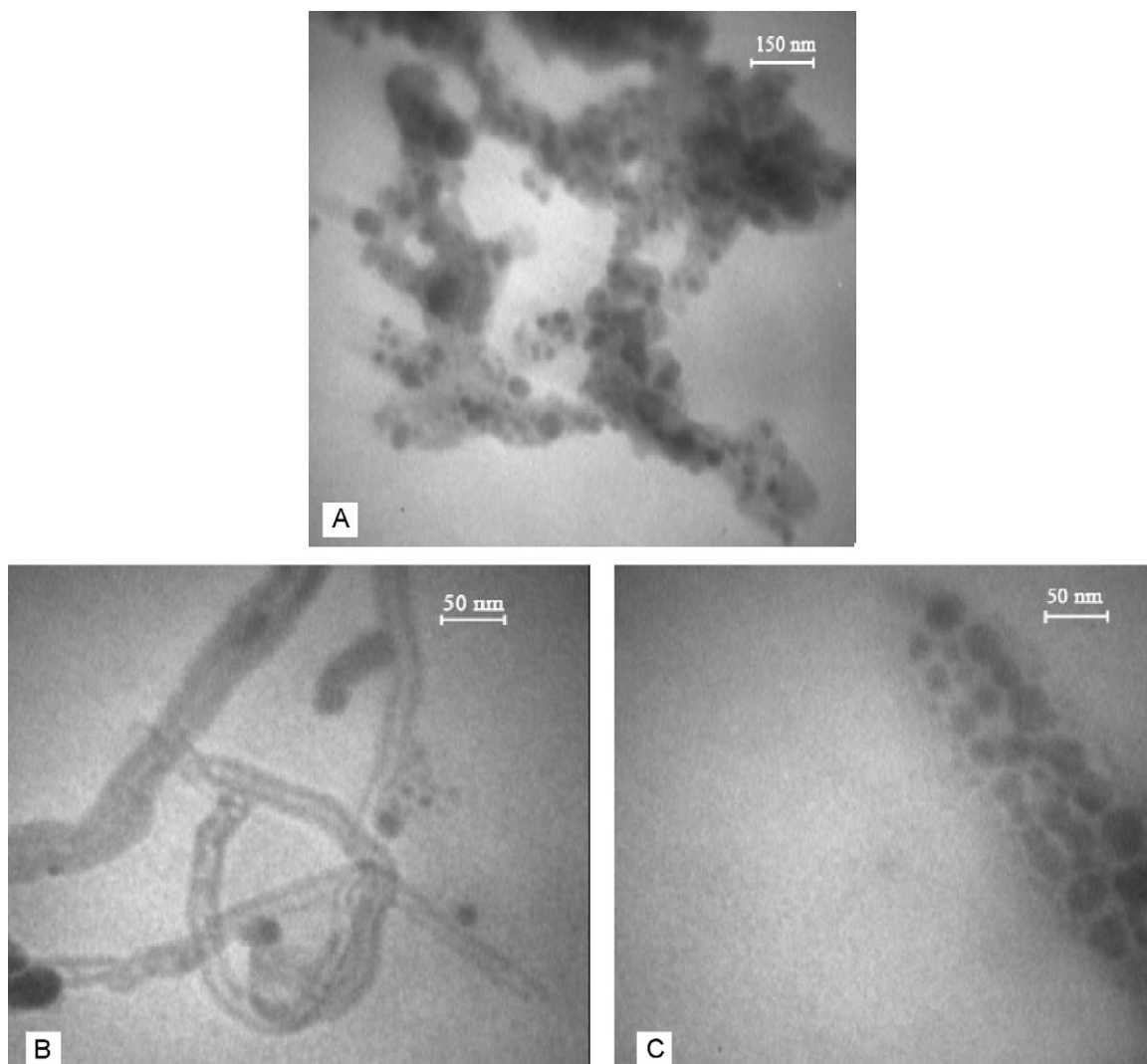
Considering high toxicity of cyanide for humans, even at very low concentration levels, the development or improvement of analytical methods for the determination of low levels of cyanide ion in aqueous environments is thus of great importance. A large number of analytical methods have been published concerning the determination of cyanide in water and wastewaters including ion-selective potentiometry [5], indirect atomic absorption spectrometry [6–9], spectrofluorimetry [10,11], molecular absorption spectrophotometry [12], chromatographic technique [13] and

capillary electrophoresis [14]. There are numerous methods for determination of cyanide in the water and wastewater samples [15]. Among these methods, nanoparticles seem to be especially suitable for determination of very low levels of cyanide. But, there are only a few studies that have been reported about application of nanoparticles for determination of cyanide [16–19]. For example, Jin et al. developed luminescence method for determination of cyanide, utilizing CdSe semiconductor quantum dots (QDs) [16,17]. Also, Sun et al. used silver nanoparticles on a piezoelectric quartz crystal (PQC) for determination of cyanide [18]. The authors reported a three-dimensional silica-gel modified GC electrode with silver nanoparticles (GE/sol-gel/AgNPs) as electrochemical sensor for determination of cyanide [19].

In the present work, nanomolar quantities of free cyanide ions are electrochemically determined using silver hexacyanoferrate nanoparticles (SHFNPs) immobilized on multiwall carbon nanotube (MWCNT) modified GC electrode (GC/MWCNT-SHFNPs). The GC/MWCNT-SHFNPs were prepared to detect cyanide based on specific reaction of cyanide ions with silver ions by square wave voltammetry technique. The electrochemical system was applicable for analysis of  $CN^-$  in industrial real samples. Significantly lower detection limit, greater analytical sensitivity and stability response of this modified electrode compare favorably to other modified electrodes employed as  $CN^-$  sensors.

\* Corresponding author. Tel.: +98 541 244 6565; fax: +98 541 244 6888.

E-mail address: [mnoroozifar@chem.usb.ac.ir](mailto:mnoroozifar@chem.usb.ac.ir) (M. Noroozifar).



**Fig. 1.** A typical TEM images of the prepared SHCFNPs nanocomposite with (A) accelerating voltage 50 kV and immobilized SHCFNPs nanocomposite on MWCNT with accelerating voltage (B) 140 kV, (C) 250 kV.

## 2. Experimental

### 2.1. Chemicals and apparatus

Multiwall carbon nanotubes, with nanotube diameters, OD = 20–30 nm, wall thickness = 1–2 nm, length = 0.5–2  $\mu\text{m}$  and purity of >95% were purchased from Aldrich and used without any pretreatment. Silver nitrate, potassium hexacyanoferrate and sodium cyanide were obtained from Merck and used as received. All other chemicals were of analytical reagent grade from Merck and used without further purification. All solutions were prepared with doubly distilled water (DDW).

Cyclic voltammetric experiments were performed using a SAMA500 Electroanalyser (SAMA Research Center, Iran). All experiments were carried out using a conventional three-electrode system with the glassy carbon (GC) electrode with 2.0 mm diameter as the working electrode substrate, a platinum wire as the auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode. Cyclic voltammetric experiments were performed in quiescent solution. Electrolyte solutions were purged with high-purity nitrogen prior to electrochemical experiments. All the measurements were performed at room temperature.

The nanoparticles size and distribution of SHCFNPs assembled on MWCNT were investigated using a Zeiss CEM 902A transmission electron microscopy (TEM).

### 2.2. Preparation of SHCFNPs

Silver hexacyanoferrate nanoparticles ( $\text{Ag}_4[\text{Fe}(\text{CN})_6]$ ) were synthesized according to Rich method [20]. First, all glassware were thoroughly cleaned in a mixture solution of  $\text{HCl}:\text{HNO}_3$  (3:1, v/v), rinsed in distilled water and air-dried prior use. In a typical synthesis, 25.0 mL of  $\text{AgNO}_3$  ( $4.0 \times 10^{-3}$  M) was added drop wise (2 drops per second) to 25.0 mL of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  ( $1.0 \times 10^{-3}$  M) (which was purged with pure nitrogen gas prior to use), in a ultrasonic bath under dark condition. After addition, the reaction mixture turned milky immediately. The mixture was sonicated further for 30 min. The solid was isolated by centrifugation and washed five times by water to remove any unreacted impurities. At the end, the solid was dispersed in 10 ml water with the aid of sonication. The concentration of nanoparticles in resulted suspension was  $2.5 \times 10^{-3}$  M. The suspension was stored at 4 °C and prevented from light. This suspension was stable for at least three weeks.

### 2.3. Electrode modification

The GC electrode was polished with 0.05- $\mu\text{m}$  alumina slurry. After rinsing with double-distilled water, it was sonicated in water and absolute ethanol for about 1 min each. Next, the GC electrode was transferred to the electrochemical cell for further cleaning by

using cyclic voltammetry between  $-0.5$  and  $+1.5$  V at a scan rate of  $100 \text{ mV s}^{-1}$  in freshly prepared deoxygenated  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  until a stable cyclic voltammetric profile was obtained. The treated electrode was dried under a nitrogen stream and used immediately for modification. The  $5 \text{ mL N,N}$ -dimethylformamide (DMF) containing  $0.5 \text{ mL}$  of SHCFNPs ( $2.5 \times 10^{-3} \text{ M}$ ) and  $2 \text{ mg}$  MWCNT was mixed under ultrasonic agitation for  $1 \text{ h}$  to form a GC/MWCNT-SHCFNPs solution. The clean GC electrode was coated by casting  $5.0 \mu\text{L}$  of the MWCNT-SHCFNPs suspension and dried under infrared radiation to form the MWCNT-SHCFNPs adsorbed GC electrode, denoted as GC/MWCNT-SHCFNPs. When not in use, the modified electrode was stored in DDW.

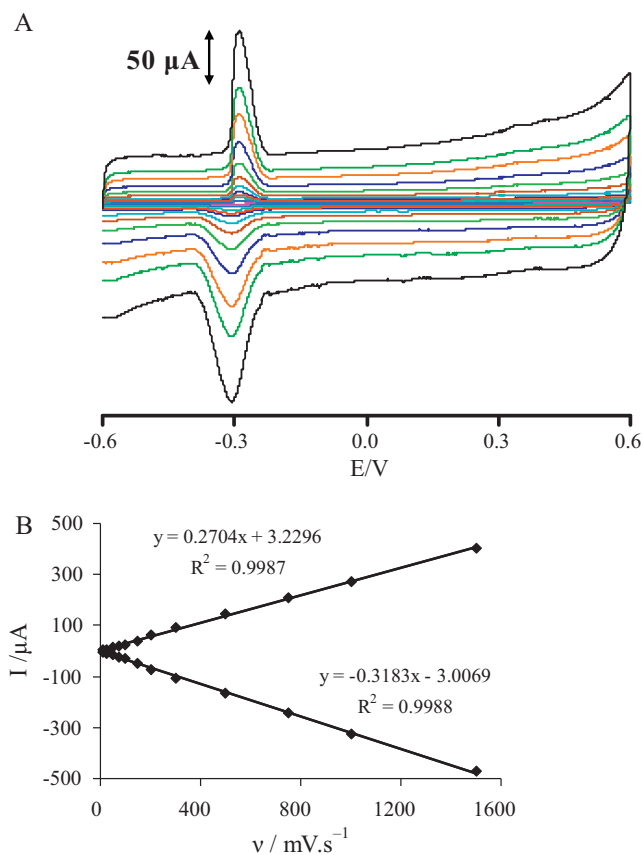
### 3. Results and discussion

#### 3.1. TEM characterization of SHCFNPs

Silver hexacyanoferrate nanoparticles are successfully prepared by sonication method, which exhibit a milk-white turbidity due to the light scattering of the nanoparticles. Fig. 1A shows the TEM images of prepared SHCFNPs, with an average diameter of around  $27 \text{ nm}$  based on the TEM measurement out of  $200$  nanoparticles. As shown in Fig. 1B and C, the attachment of nanoparticles onto multi-walled carbon nanotube was successful, and the carbon nanotube was surrounded with abundant nanoparticles.

#### 3.2. Electrochemical characteristics of modified electrode

Fig. 2A shows the cyclic voltammograms (CVs) of the resulting electrode obtained in borax buffer solution (BBS) with pH 8.0



**Fig. 2.** (A) Cyclic voltammograms of the GC/MWCNT-SHCFNPs electrode in BBS with pH 8.0 ( $0.1 \text{ M}$ ) and at various scan rates (from inner to outer curve):  $10, 25, 50, 75, 100, 150, 200, 300, 500, 750, 1000$  and  $1500 \text{ mV s}^{-1}$ . (B) Plots of peak currents vs. scan rates.

( $0.1 \text{ M}$ ) and in various potential sweep rates. The electrochemical response of AgHCFNPs exhibited a pair of well-defined redox peaks with a formal potential of  $-0.298 \text{ V}$  vs. SCE, and small potential peak separation  $\Delta E_p = 18 \text{ mV}$  which can be attributed to the electron transformations between Fe(II) and Fe(III) in the nanoparticles. The reaction of these voltammograms is as follows:



Eq. (1) includes the oxidation and reduction of  $\text{Ag}_4[\text{Fe}(\text{CN})_6]$  ( $\text{Fe}^{\text{II}}$ ) and production of  $\text{Ag}_3[\text{Fe}(\text{CN})_6]$  ( $\text{Fe}^{\text{III}}$ ) with loss of one electron in anodic sweep.

As shown in Fig. 2B, the peak currents increased linearly with the scan rate between  $10$  and  $1500 \text{ mV s}^{-1}$  as expected for a surface process. Moreover, the anodic peak currents were almost the same as the corresponding cathodic peak currents and the peak potential did not change with increasing scan rate. As shown in Fig. 2B,  $I_{pa}$  and  $I_{pc}$  were linearly dependent on scan rate, as expected for surface confined redox process. And the ratio of the anodic peak current to the cathodic peak current  $I_{pc}:I_{pa}$ , is almost close to unity. These behaviors are consistent with a diffusionless system, reversible electron transfer process [21].

An approximate amount of the electroactive species can be estimated by the method suggested by Sharp et al. [22]. According to this method, the peak current is related to the surface concentration of electroactive species,  $\Gamma$ , by Eq. (2):

$$I_p = \frac{n^2 F^2 A \Gamma v}{4RT} \quad (2)$$

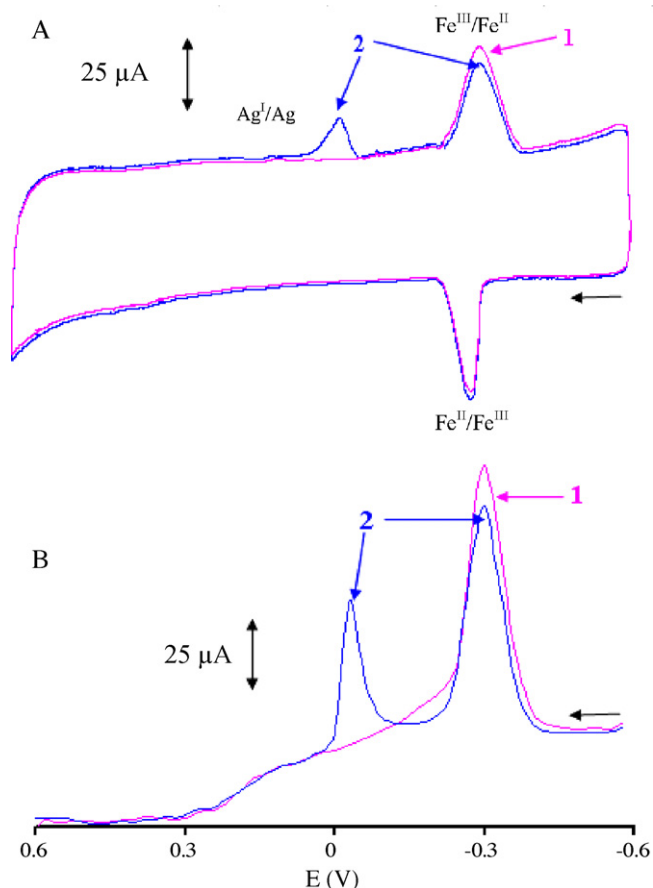
Here  $n$  represents the number of electrons involved in the reaction,  $A$  is the geometric surface area ( $0.0314 \text{ cm}^2$ ) of the electrode,  $\Gamma$  ( $\text{mol cm}^{-2}$ ) the surface coverage,  $v$  the scan rate;  $R$  ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $F$  ( $96485 \text{ C mol}^{-1}$ ) and  $T$  ( $298 \text{ K}$ ) denote the gas constant, the temperature, and the Faraday constant, respectively. From the slope ( $0.270$ , from Fig. 2B) of the plot of anodic peak currents vs. scan rates, the surface concentration of SHCFNPs was calculated to be  $9.17 \times 10^{-9} \text{ mol cm}^{-2}$  for  $n = 1$ .

#### 3.3. Electrochemical behavior of $\text{CN}^-$ at GC/MWCNT-SHCFNPs modified electrode

The prime objective of the present work is the determination of  $\text{CN}^-$  using GC/MWCNT-SHCFNPs modified electrode. Fig. 3 shows the CVs obtained for GC/MWCNT-SHCFNPs modified electrodes in  $0.1 \text{ M}$  borax buffer solution (BBS) with pH 8.0 containing  $0.05 \text{ M}$   $\text{KNO}_3$  in the absence and presence of  $5.0 \mu\text{M}$   $\text{CN}^-$ . As shown in Fig. 3A, when  $\text{CN}^-$  was added to the solution, a new cathodic peak (in curve 2) was generated in potential  $-0.044 \text{ V}$  (vs. SCE). Fig. 3B indicates similar phenomenon by the square wave voltammetry (SWV) mode when cyanide was added to the electrochemical cell and potential sweep was from  $-0.6$  to  $0.6 \text{ V}$  (vs. SCE). As shown in Fig. 3B, when  $\text{CN}^-$  was added to the solution, a new peak (in curve 2) was generated in half potential ( $E_{1/2}$ )  $-0.034 \text{ V}$  (vs. SCE). The corresponding reactions of these voltammograms can be explained as follows:



Cyanide can react with SHCFNPs (reaction (3)) [23] and produces  $\text{Ag}(\text{CN})_2^-$  complex ( $\text{Ag}^{\text{I}}$ ) which can be reduced to  $\text{Ag}$  in an electrochemical reaction in  $E^\circ = -0.31 \text{ V/SHE}$  or  $E^\circ = -0.068 \text{ V/SCE}$  (reaction (4)) [24].



**Fig. 3.** (A) Cyclic and (B) square wave voltammograms of a GC/MWCNT-SHCFNPs in  $0.1 \text{ mol L}^{-1}$  of BBS at pH 8.0 in the (1) absence and (2) presence of cyanide ( $5.0 \mu\text{M}$ ), scan rate;  $100 \text{ mV s}^{-1}$ .

### 3.4. Optimization of experimental conditions

The composition of the modified electrode was optimized by comparing the square wave voltammetric response of different amounts of MWCNT to different volumes of SHCFNPs suspension in BBS  $0.1 \text{ M}$  (pH 8.0) containing  $5.0 \mu\text{M CN}^-$ . The best composition is defined as the composition by which maximum decrease in  $I_{pc}$  for  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  or maximum increase in  $I_{pc}$  for reduction  $\text{Ag}(\text{CN})_2^-/\text{Ag}$  ( $\text{Ag}^+/\text{Ag}$ ) is achieved. For this purpose a series of experiments were carried out at above-mentioned conditions. The results are shown in Table 1. According to Table 1, when glassy carbon electrode was coated with  $5 \mu\text{L}$  of a mixture containing  $2 \text{ mg}$  MWCNT and  $0.5 \text{ ml}$  SHCFNPs suspension in  $5 \text{ mL}$  DMF, maximum decrease in  $I_{pc}$  for  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  or maximum increase in  $I_{pc}$  for reduction of  $\text{Ag}(\text{CN})_2^-$  to

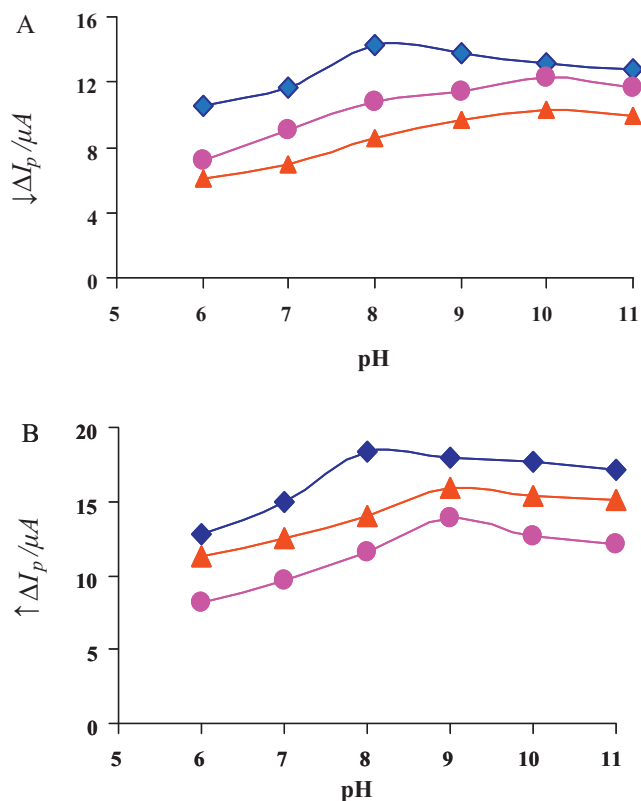
**Table 1**

Decrease in  $I_p$  ( $\downarrow \Delta I_p$ ) for  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  or increase in  $I_p$  ( $\uparrow \Delta I_p$ ) for  $\text{Ag}/\text{Ag}^+$  for compositions with different ratios of mg MWCNT/mL SHCFNPs in BBS (pH 8.0) containing  $5.0 \mu\text{M CN}^-$ . Scan rate,  $100 \text{ mV s}^{-1}$ .

mg CNT/mL AgHCFNPs	( $\uparrow \Delta I_p$ ) <sup>a</sup> / $\mu\text{A}$	( $\downarrow \Delta I_p$ ) <sup>b</sup> / $\mu\text{A}$
0.5/0.5	7.1	5.5
1.0/0.5	12.4	8.0
2.0/0.25	5.2	2.7
2.0/0.50	18.5	14.6
2.0/1.0	15.3	12.9
3.0/0.5	17.2	13.4
4.0/0.5	14.9	11.1
5.0/0.5	12.2	9.7

<sup>a</sup> Increase in  $I_{pc}$ .

<sup>b</sup> Decrease in  $I_{pc}$ .



**Fig. 4.** Effect of pH on the cyanide determination. (♦) Borax, (▲) bicarbonate, and (●) universal buffer solution.  $\text{CN}^-$  concentration is  $5.0 \mu\text{M}$ . (A)  $\uparrow \Delta I_p$  and (B)  $\downarrow \Delta I_p$  are same as described in Table 1.

$\text{Ag}$  was obtained. If the MWCNT content in the modificative mixture was too high ( $>3 \text{ mg}$ ) or too low ( $<1 \text{ mg}$ ), then the sensitivity was low due to the presence of a large background current or insufficient amount of the MWCNT for adhesion nanoparticles to the glassy carbon electrode surface, respectively. In the latter case, modificative film was removed from the electrode's surface, easily.

The effect of solution pH on the electrochemical response of the GC/MWCNT-SHCFNPs towards the determination of  $\text{CN}^-$  was studied between 6.0 and 11.0 with a chosen cyanide concentration of  $5.0 \mu\text{M}$  for each pH value. A series of buffer solutions including universal buffer ( $0.1 \text{ M CH}_3\text{COOH}$ ,  $0.1 \text{ M H}_3\text{PO}_4$ , and  $0.1 \text{ M H}_3\text{BO}_3$ ), bicarbonate buffer solution ( $0.1 \text{ M NaHCO}_3$ ) and borax buffer solution ( $0.1 \text{ M Na}_2\text{B}_4\text{O}_7$ ) were prepared and pHs were adjusted using NaOH or HCl in the range from 6.0 to 11.0. As shown in Fig. 4A and 4B, the decreasing and increasing in cathodic peak current in borax buffer solution with pH 8.0 is the highest value and it was chosen as the optimum pH. **Caution!** Because of converting of  $\text{CN}^-$  to HCN at pHs below 6, degassing of solution with nitrogen must not be used.

## 4. Analytical utility

### 4.1. Calibration curve, linear range and detection limit of the method

In order to minimize background currents and further improve the detection sensitivity, square wave voltammetry was applied to the detection of cyanide in synthetic laboratory standard solutions and industrial wastewater samples. Fig. 5 is shown a typical square wave voltammograms of GC/MWCNT-SHCFNPs modified electrode with increasing cyanide concentration under the optimized conditions. As shown in Fig. 5, two calibration curves were obtained for



**Table 2**  
Comparison of the proposed method with other electroanalytical methods for cyanide determination.

Electrochemical method	Sample	Linear range (mol L <sup>-1</sup> )	Detection limit (mol L <sup>-1</sup> )	RSD %	Ref.
Cyclic voltammetry	Industrial wastewater	$1.5 \times 10^{-6}$ to $2.1 \times 10^{-4}$	$1.4 \times 10^{-8}$	2.6	[19]
Amperometric sensor	Physiological solutions	Up to $120.0 \times 10^{-6}$	$3.8 \times 10^{-6}$	–	[27]
Differential pulse polarography (DPP)	Blood plasma	$2.3 \times 10^{-6}$ to $1.9 \times 10^{-5}$	$1.5 \times 10^{-6}$	9	[28]
Adsorptive stripping voltammetry	Industrial wastewater	$5.0 \times 10^{-8}$ to $8.0 \times 10^{-7}$	$1.0 \times 10^{-8}$	4	[29]
Square wave voltammetry	Industrial wastewater	$4.0 \times 10^{-8}$ to $9.9 \times 10^{-5}$	$8.3 \times 10^{-9}$	1.4	This work

determination of cyanide; one based on increase in Ag/Ag<sup>I</sup> redox peak current (Fig. 3B, second peak in curve 2) and another based on decrease in Fe<sup>II</sup>/Fe<sup>III</sup> anodic peak current (Fig. 3B, first peak in curve 2). Also, in Fig. 5 an isopotential point (IPP) is observable at ca. -0.110 V which flags the presence of a mixture of two species [25]. As mentioned above, these two species are consistent to Ag<sub>4</sub>Fe(CN)<sub>6</sub> and Ag(CN)<sub>2</sub><sup>-</sup>.

As indicated from the resulting calibration plots (Fig. 6), increasing in Ag/Ag<sup>I</sup> anodic peak current provides a more sensitive and wider calibration curve with higher correlation coefficient, and therefore it was chosen as analytical signal for cyanide determination. It was found that the  $\uparrow\Delta I_p$  of Ag/Ag<sup>I</sup> is proportional to cyanide concentration over the range of  $4.0 \times 10^{-8}$  to  $1.5 \times 10^{-4}$  M (40.0 nM to 150.0  $\mu$ M). The correlation coefficient (*r*) and the equation for calibration graphs were shown in Fig. 5B. The high intercept may be related to the strong background current which accompanied with MWCNT. The detection limit (DL,  $Y_{LOD} = \bar{X}_B + 3S_B$ , where  $Y_{LOD}$  is the signal for detection limit,  $\bar{X}_B$  the mean of blank signal and  $S_B$  the standard deviation of blank signal) [26] was obtained as  $8.3 \times 10^{-9}$  M (8.3 nM). A comparison of the analytical param-

**Table 3**  
The effects of various possible interference ions on the analysis of 5.0  $\mu$ M cyanide.

Interfere ion	Tolerance limit
S <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , and CO <sub>3</sub> <sup>2-</sup>	500
Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , and Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	450
Cr <sup>3+</sup> , Br <sup>-</sup> , and Cu <sup>2+</sup>	200
S <sub>2</sub> O <sub>5</sub> <sup>2-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	100
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , Hg <sup>2+</sup>	80
CrO <sub>4</sub> <sup>2-</sup> , I <sup>-</sup>	50
SO <sub>3</sub> <sup>2-</sup> , SCN <sup>-</sup> , N <sub>3</sub> <sup>-</sup> , and PO <sub>4</sub> <sup>3-</sup>	30

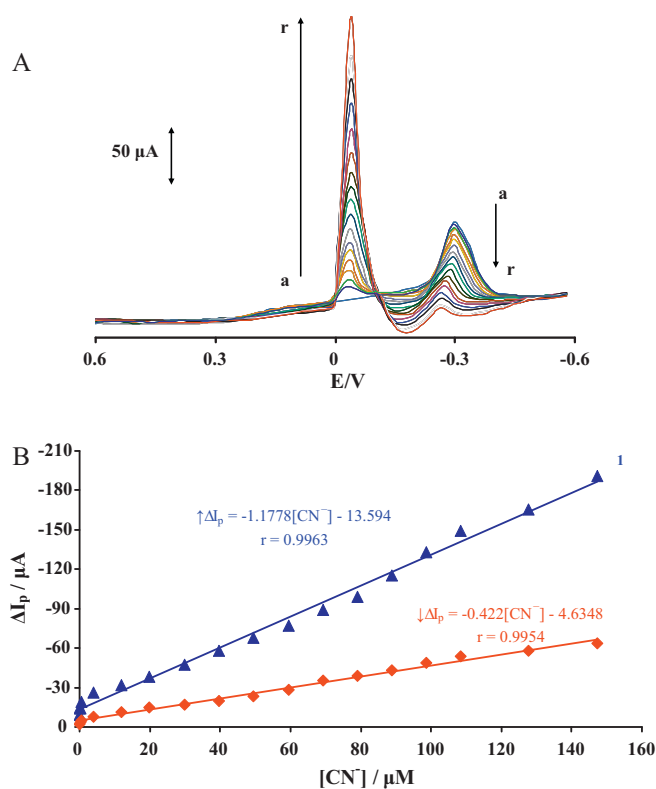
eters obtained at the GC/MWCNT-SHCFNPs modified electrode with those of electrochemical methodologies currently available for cyanide detection [19,27–29] (Table 2) reveals that the detection limit of  $8.3 \times 10^{-9}$  M compares favorably with those reported for these procedures.

#### 4.2. Interferences study

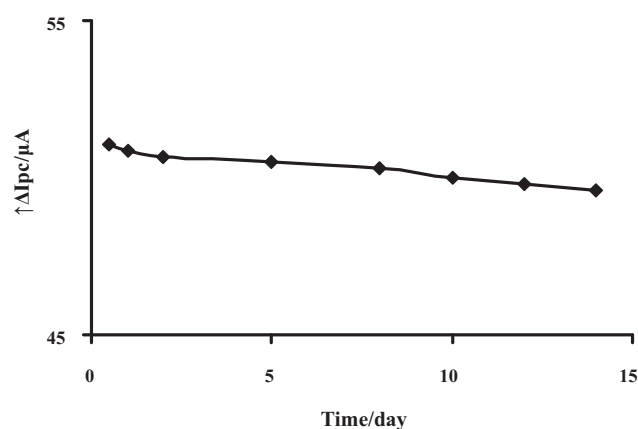
The effect of various interferences concurrently presented in wastewaters for the determination of 5.0  $\mu$ M cyanide using the proposed method was investigated. The tolerance limit was taken as the amount which caused an error of  $\pm 5\%$  in signal. The results are summarized in Table 3. Almost all the ions examined did not interfere with cyanide in electroplating wastewater samples and it was used as a criterion for the selectivity of the modified electrode.

#### 4.3. Reproducibility, stability and recovery test of the modified electrode

The reproducibility of the electrode was determined. The reproducibility of the current response for the modified electrode was examined at a CN<sup>-</sup> concentration of 5.0  $\mu$ M. The relative standard deviation is 1.4% for seven successive assays (Table 4). The long time stability of the modified electrode was important. It was remarkable that after two weeks the electrode retained 97.2% of the initial sensitivity to cyanide (Fig. 6). Good response reproducibility and good long time stability may be explained by the fact that the



**Fig. 5.** (A) Typical square wave voltammograms obtained at the modified electrode with different concentration of cyanide, (a–r)  $0.0 \times 10^{-8}$ ,  $4.0 \times 10^{-8}$ ,  $8.0 \times 10^{-8}$ ,  $2.0 \times 10^{-7}$ ,  $4.0 \times 10^{-7}$ ,  $4.0 \times 10^{-6}$ ,  $1.2 \times 10^{-5}$ ,  $2.0 \times 10^{-5}$ ,  $3.0 \times 10^{-5}$ ,  $4.0 \times 10^{-5}$ ,  $5.0 \times 10^{-5}$ ,  $6.0 \times 10^{-5}$ ,  $7.0 \times 10^{-5}$ ,  $8.0 \times 10^{-5}$ ,  $8.9 \times 10^{-5}$ ,  $9.8 \times 10^{-5}$ ,  $1.1 \times 10^{-4}$ ,  $1.3 \times 10^{-4}$ , and  $1.5 \times 10^{-4}$  mol L<sup>-1</sup>. (B) Calibration plots for cyanide determination based on (1) increasing and (2) decreasing cathodic peak currents. Square wave voltammetric parameters were as follows: step potential, 20 mV; pulse amplitude, 50 mV; and frequency, 5 Hz.



**Fig. 6.** Variation of electrode response to the cyanide ( $[CN^-] = 5.0 \mu$ M) during two weeks.

**Table 4**  
Data obtained for reproducibility test.

Assay number	$\uparrow \Delta I_{pc}/\mu A$
1	50.14
2	51.03
3	50.78
4	50.06
5	49.64
6	51.32
7	49.53

**Table 5**  
Results of recovery tests.

Sample	[CN <sup>-</sup> ] added (μM)	[CN <sup>-</sup> ] found (μM)	Recovery (%)
Gold industrial electrolyte bath Solution 1	0.00	4.75	–
	4.00	8.92	104.2
Gold industrial electrolyte bath Solution 2	0.00	6.19	–
	8.00	14.12	99.1
Copper industrial electrolyte bath Solution	0.00	0.73	–
	4.00	4.67	98.5
Brass industrial electrolyte bath Solution	0.00	3.20	–
	8.00	11.28	101.0

SHCFNPs are uniformly and firmly attached to the MWCNT and cannot separate from it during potential sweep.

The recovery of the spiked samples is in the range of 98.5–104.2%, indicating that the detection procedures are free from interferences of the industrial wastewater samples matrix (Table 5).

#### 4.4. Application to industrial samples

The proposed method was applied for the determination of cyanide in different kinds of industrial effluent. The obtained results were compared with the procedure developed by Lambert et al. [30,19]. In the Lambert method the absorbance of the product is registered as the analytical signal. Table 6 lists the results obtained upon application of the proposed method. The obtained results were compared with those provided by the Lambert's method by the paired *t*-test [26]. The paired *t*-test equation applied in statistics is  $t = \bar{d}\sqrt{n}/s_d$ , where  $\bar{d}$  and  $s_d$  are the mean and standard deviation, respectively, of *d* (the difference between paired values). For the pair of values in Table 6,  $\bar{d}$  is  $4.2 \times 10^{-7}$  and  $s_d$  is  $1.89 \times 10^{-6}$ . The calculated *t* was found to be 0.737. The critical value of *t*

**Table 6**  
Analysis of sample from different industrial electroplating wastewaters (average of five replicates).

Sample (electroplating wastewater)	Proposed method (mol L <sup>-1</sup> )	Standard method (mol L <sup>-1</sup> )
Gold industrial electrolyte bath solution 1	$4.75 \times 10^{-6} \pm 7.3 \times 10^{-7}$	$4.36 \times 10^{-6} \pm 5.0 \times 10^{-7}$
Gold industrial electrolyte bath solution 2	$6.19 \times 10^{-6} \pm 1.1 \times 10^{-6}$	$6.24 \times 10^{-6} \pm 2.7 \times 10^{-7}$
Copper industrial electrolyte bath solution	$7.32 \times 10^{-7} \pm 1.2 \times 10^{-7}$	$7.65 \times 10^{-7} \pm 8.1 \times 10^{-8}$
Brass industrial electrolyte bath solution	$3.20 \times 10^{-6} \pm 4.9 \times 10^{-7}$	$3.42 \times 10^{-6} \pm 3.0 \times 10^{-7}$

(tabulated *t*) for *n* – 1 degrees of freedom (in this work 3) is 3.18 (*P* = 0.05), since the calculated value of *t* is less than this. So, the null hypothesis is not rejected: the methods do not give significantly different results for cyanide concentration. These results showed good agreement with the results obtained by the standard method.

## 5. Conclusions

Silver hexacyanoferrate nanoparticles were easily prepared and used for modification of a glassy carbon electrode. SHCFNPs were characterized by TEM and cyclic voltammetry. The GC/MWCNT-SHCFNPs electrode was used for determination of CN<sup>-</sup> based on the specific reaction of cyanide ions and SHCFNPs. When CN<sup>-</sup> was added to the electrochemical cell due to the reverse and concurrent changes in cathodic peak currents of Ag<sub>4</sub>[Fe(CN)<sub>6</sub>] and Ag(CN)<sub>2</sub><sup>-</sup> reduction an isopotential point was generated. The electrochemical system was applicable for the analysis of CN<sup>-</sup> in industrial real samples. Significantly lower detection limit (8.3 nM), greater analytical sensitivity and stability response of this modified electrode compare favorably to other modified electrodes employed as CN<sup>-</sup> sensors. Furthermore, the new protocol compares favorably with existing electrochemical procedures in terms of simplicity and economy of electrode preparation.

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