

Full Paper

Cobalt-graphene Nanocomposite Electrode for Phosphate Sensing

Kazem Kargosha, Payam Hemmatkhah and Seyyed Hamid Ahmadi*

Chemistry & Chemical Engineering Research Center of Iran, Tehran, Iran

*Corresponding Author, Tel.: +982144787972; Fax: +982144787707

E-Mail: ahmadi@ccerci.ac.ir

Received: 31 January 2017 / Accepted: 15 May 2017/ Published online: 15 August 2017

Abstract- Cobalt-decorated graphene nanocomposite electrode was prepared via an electrochemical strategy and utilized for phosphate sensing. Electrochemical approach has found to be a simple, cheap, and green method for this purpose. The composite electrode was also characterized with scanning electron microscopy and cyclic voltammetry. Characteristics such as potentiometric response, calibration curve, response time, effects of dissolved oxygen, interfering ions, and pH were also evaluated. The potentiometric response for the range of 10^{-6} to 10^{-2} M showed a good linear relationship with the logarithm of phosphate concentrations with a slope of -31.6 mV per decade change of concentration.

Keywords- Potentiometric Sensor, Phosphate, Water Analysis, Graphene-Cobalt Nanoparticles

1. INTRODUCTION

Phosphate is a known contaminant of ground and surface water and is present almost everywhere. For decades, phosphate has been the subject of continued research. Phosphate analysis has been always important in various fields such as environment, agriculture, clinical, and also industrial water analyses. In environmental analysis, phosphate is regarded as the major source of eutrophication of rivers and lakes [1-2]. In clinical research, Phosphate concentrations in body fluids are related to Hyperparathyroidism, Vitamin D deficiency, and Fanconi syndrome [3-4]. Monitoring of phosphate in soil extract is another highly desired application for sensing phosphate levels in fertilizers to serve the agricultural science. The

diversity of applications and examples represents a significant need for development of fast, simple, sensitive and also cost-effective phosphate sensors which enable assessment and determination of phosphate in various systems.

Many techniques have been suggested in the literature to fabricate phosphate sensors, and significant effort has been focused on the development of phosphate-selective electrodes [5-8]. Xiao et al. [9] suggested cobalt as a phosphate-sensitive electrode material and showed that oxidized surfaces of metallic cobalt exhibits a potentiometric response towards phosphate ion. It was suggested that the formation of cobalt phosphate will affect the mixed potential of the cobalt electrode. Hence, the shift of the potential will be proportional to phosphate concentration based on the Nernst's equation. The ultrapure cobalt wire has also been used as a stable sensitive phosphate sensor by Chen et al [10]. Others who have used cobalt as phosphate sensing agent include Kim [11], Wang [12], Lee et al. [13], and Meruva [14].

Graphene-based materials, Graphene oxide (GO) and reduced graphene oxide (RGO), have recently attracted tremendous interest in electrochemical sensing due to unique properties [15-16]. Chemical inertness, potential window and enhanced electrochemical activity in a variety of redox reactions are the most important properties for electrochemical applications and enable graphene materials to be used as electrochemical transducer, focusing on the chemical interaction between graphene and the targeted analyte [17-18]. Electrochemical synthesis and specifically electrodeposition with the advantages of low cost, low synthetic temperature, high purity, simplicity, and environmental friendliness has been regarded as a highly efficient method for the fabrication of nanostructured materials and composite electrodes.

In this paper, an electrochemical approach to fabricate a graphene-cobalt nanoparticles composite electrode on the glassy carbon electrode indicated as GCE-RGO-Co NPs is examined. Besides, the performance of the composite electrode evaluated for determination of phosphate. The fabrication process consists of electrodeposition of graphene oxide (GO) on glassy carbon electrode (GCE) and electroreduction to reduced graphene oxide (RGO) followed by electrosynthesis of cobalt nanoparticles on the GCE-RGO electrode.

2. EXPERIMENTAL

2.1. Chemicals and reagents

Working standard solutions of KH_2PO_4 (Sigma-Aldrich, USA) with concentrations of 10^{-8} to 10^{-2} M were prepared by diluting stock standard solution which was made by dissolving appropriate amount of phosphate in ultra-pure water. Graphene oxide, GO powder (XG sciences, USA) was used as a 3 mg mL^{-1} aqueous solution. Cobalt Chloride (CoCl_2), Boric acid (H_3BO_3), Potassium chloride (KCl) was also purchased from Merck KGaA, Germany.

All chemicals were of analytical grade and used without any further purification. All solutions were prepared with ultra-pure water ($18.2 \text{ M}\Omega\text{cm}$), purified by a Millipore-Q-system (Millipore, USA).

2.2. Instrumentation

All electrochemical measurements were performed on a 2065 electrochemical workstation (Behpazouh, Iran) at the ambient temperature. A conventional three-electrode system was employed including a bare or modified GCE as working electrode, a platinum wire as auxiliary electrode and a Ag/AgCl saturated KCl as reference electrode. The cyclic voltammetric experiments were carried out under a continuous stirring. The supporting electrolyte solution was purged with high purity argon (99.999%) for 15 min prior to each measurement and then an argon atmosphere was kept over the solution during measurements. Potential recording was carried out by pH/millivoltmeter (Metrohm 780, Switzerland). Scanning electron microscopy was done with Vega3 (Tescan, Czech Republic).

2.3. Fabrication of the Composite electrode

As mentioned earlier, the whole fabrication procedure is based on the electrochemical approach. The glassy carbon electrode (GCE) was polished carefully and then cleaned by sonication in water for 15 minutes. Prior to electrodeposition, the polished GCE was immersed into 3 mg mL^{-1} aqueous solution of graphene oxide and cyclic voltammetry was performed in the graphene oxide dispersion with a magnetic stirring and argon bubbling in a three electrode system where platinum wire and Ag/AgCl saturated KCl used as auxiliary and reference electrodes, respectively. Bare glassy carbon electrode (GCE) acted as the working electrode. After electrodeposition, the electrode was rinsed with ultra-pure water to remove the unattached graphene.

In the following step, the graphene modified glassy carbon electrode (GCE-RGO) was immersed in cobalt chloride (0.05 M), potassium chloride (0.10 M), and boric acid (0.20 M) solutions and a cyclic scan in the potential range of 0.5 V to -1.5 V was performed to deposit the cobalt nanoparticles on the graphene modified electrode. For electrochemical behavior comparison, cobalt nanoparticles were also electrodeposited on the bare glassy carbon electrode.

3. RESULTS AND DISCUSSION

3.1. Electrodeposition of GO and Co NPs

Fig. 1 shows the cyclic voltammograms of graphene oxide electrodeposited on glassy carbon electrode, where one anodic peak at 0.45 V and two cathodic peaks at -0.25 V and -1.00 V are observed.

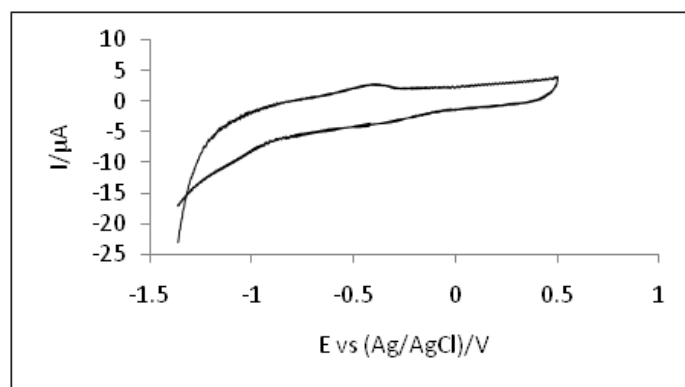


Fig. 1. CV of 3.0 mg mL⁻¹ aqueous graphene oxide at 50 mV s⁻¹

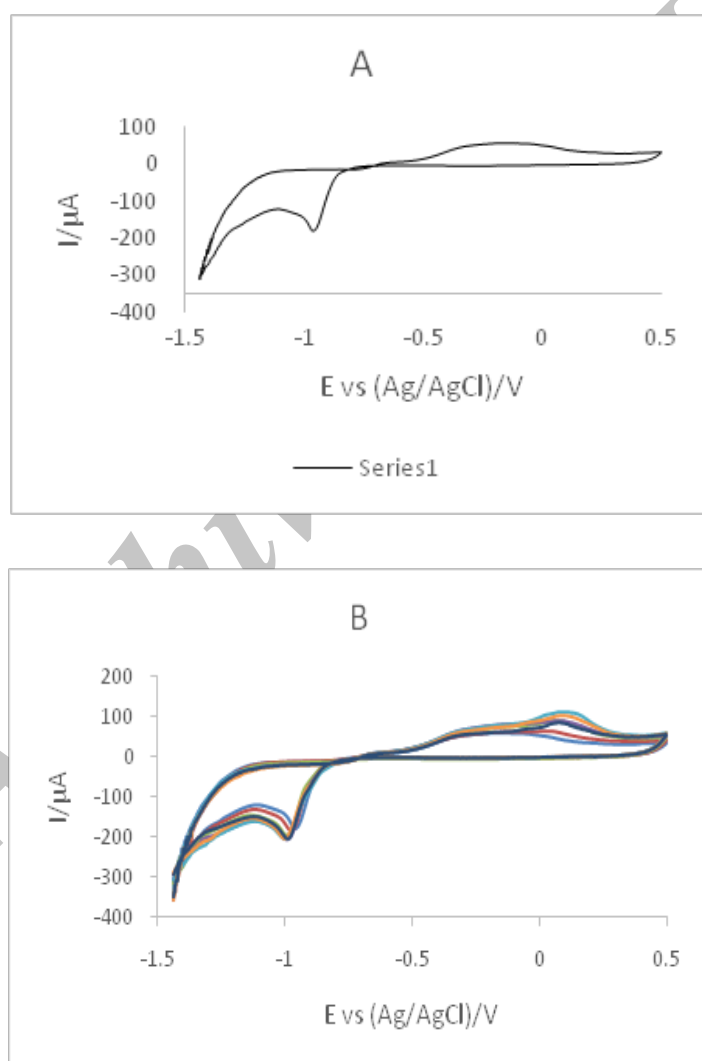


Fig. 2. (A) CVs of GCE-RGO in 0.2 M KCl , H₃BO₃, and 0.005 M CoCl₂ at 50 mV s⁻¹; (B) successive CV scans at 50 mV s⁻¹

The peaks at 0.45 V and -0.25 V are related to redox pair of oxygen-containing groups on graphene oxide that are not reduced by cyclic voltammetry. The cathodic peak at -1.00 V is attributed to irreversible electroreduction of graphene oxide [11-14].

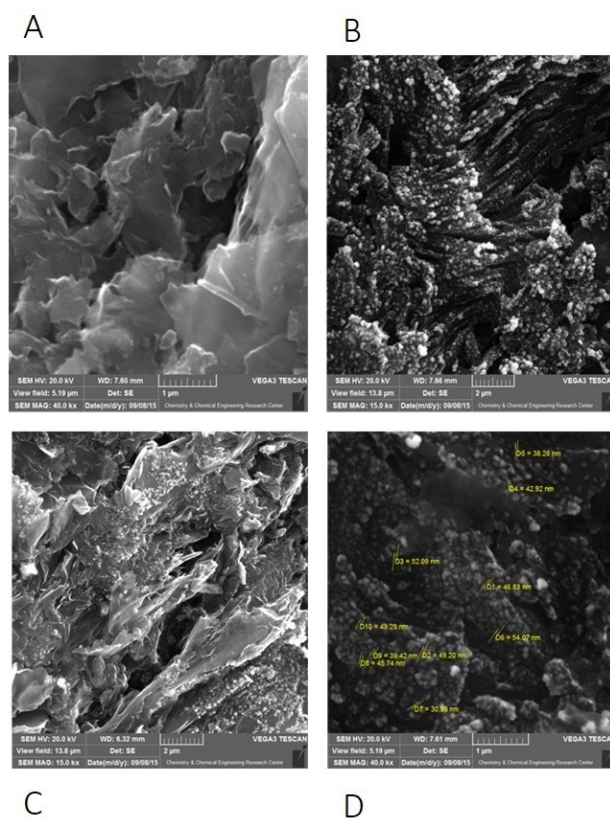


Fig. 3. SEM images of GCE-RGO (A) and GCE-RGO-Co NPs (B, C, and D)

Cyclic voltammetry (CV) was also utilized to synthesize and deposit cobalt nanoparticles on the graphene modified electrode Fig. 2. Showed the cyclic voltammograms of the graphene modified electrode scanned in potential range from -1.5 V to $+0.5$ V. There was a cathodic peak at -0.85 V which resulted from the reduction of Co^{2+} on the electrode surface to form cobalt nanoparticles. As the number of scan cycle increases, the current of cathodic peak gradually decreases, and the peak potential shifts positively as indicated by the black arrow. The current decrease of cathodic peak with increasing cycle number indicated that Co^{2+} have been reduced and gradually deposited on the surface of graphene electrode.

3.2. Characterization of the composite electrodes

Fig. 3 shows the SEM image of GCE-RGO and GCE-RGO-Co NPs electrodes obtained, which clearly indicated that the graphene has deposited on the surface and provided a large surface area to the formation of cobalt nanoparticles. EDX was also applied to study the composition of the GCE-RGO-CoNPs and GCE-Co NPs composite electrodes (Fig. 4). It was

revealed that the percent of Co Nps on the GCE-RGO is almost three times higher than bare GCE which can affect the electrochemical behavior of the electrodes towards phosphate ion.

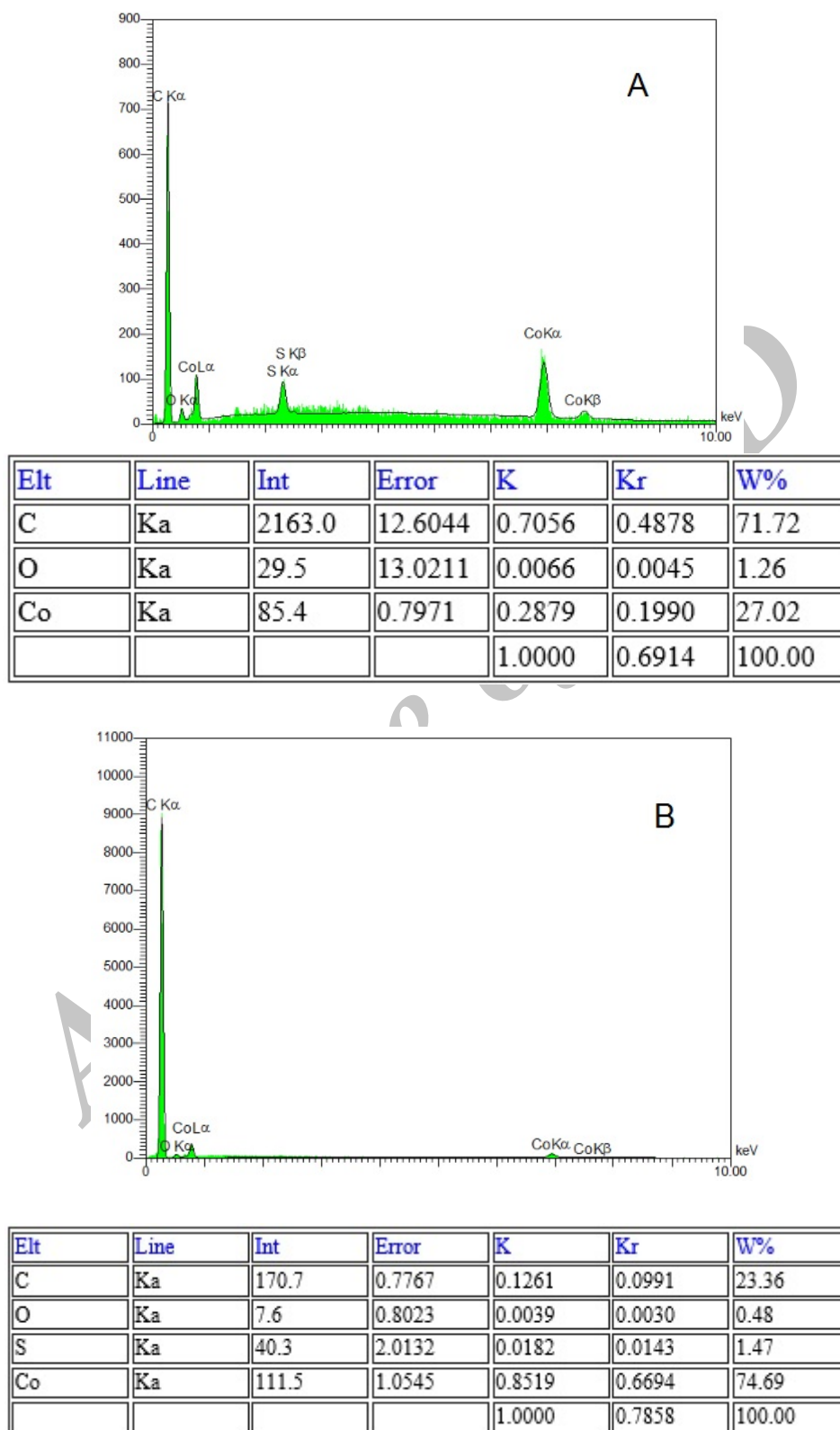


Fig. 4. EDX spectra of (A) GCE-RGO-Co NPs and (B) GCE-Co NPs composite electrodes

3.3. Electrochemical behavior

As mentioned earlier, for investigating of graphene effect on the electrode performance, the same electrodeposition procedure for cobalt nanoparticles on the glassy carbon electrode was also carried out. The electrochemical behaviors of GCE, GCE-Co NPs, and GCE-RGO-Co NPs electrodes were investigated by cyclic voltammetry in 10^{-5} M phosphate solution (Fig. 5). It is evident from voltammogram that GCE-RGO-Co NPs composite electrode indicates an anodic peak with much higher current than GCE-RGO-Co NPs. This result is in good agreement with the EDX spectra of the GCE-Co and GCE-RGO-Co stated the larger loading capacity of RGO in comparison with GCE. The large surface-to-volume ratio of the Co NPs provided by graphene increases the probability of contact to phosphate ions and hence improves the electrochemical response.

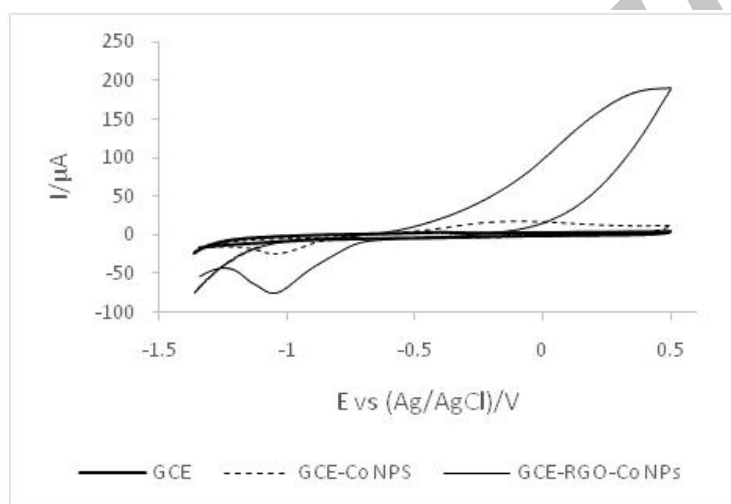


Fig. 5. CVs of the three electrodes in the 10^{-5} M phosphate solution at 50 mV s^{-1}

3.4. Potentiometric Response

3.4.1. Calibration

To construct the calibration curve, nine working standard solutions of phosphate with concentrations of 10^{-8} - 10^{-2} M were analyzed and potentiometric response of GCE-RGO-Co NPs composite electrode toward phosphate ions were recorded (see Fig. 6). According to Fig. 6, the GCE-RGO-Co NPs composite electrode showed a very good potentiometric response towards phosphate ions. The potentiometric response for the range of 10^{-6} to 10^{-2} M showed a good linear relationship with the logarithm of phosphate concentrations with a slope of -31.6 mV per decade change of concentration and R^2 value of 0.99.

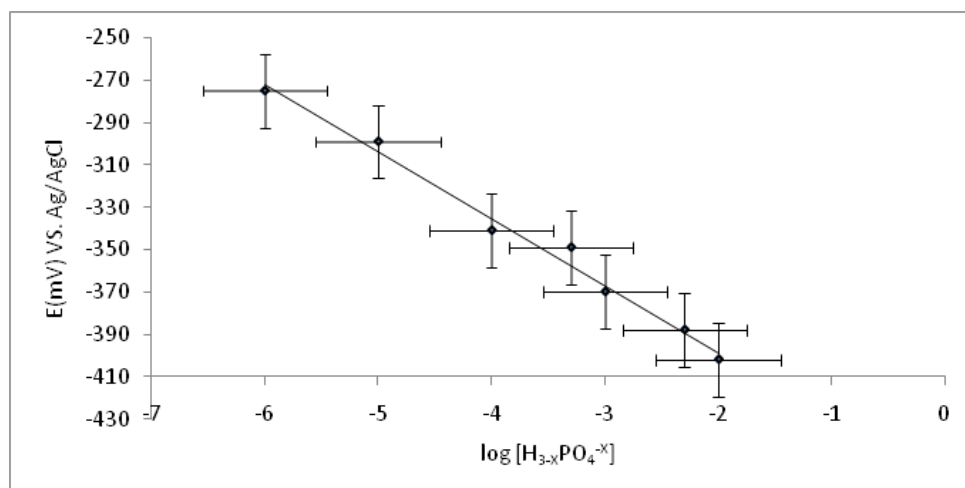


Fig. 6. Potentiometric response of GCE-RGO-Co NPs composite electrode

3.4.2. Response time

The response time of the electrode was tested by measuring required time to achieve a steady state potential (within ± 1 mV) after successive immersion of the electrode in a series of phosphate solutions, each having a 10-fold increase in concentration from 10^{-6} to 10^{-3} of phosphate ion. The composite electrode yielded steady potentials within 15 s. the potential readings stays stable for at least nine minutes (Fig. 7). In order to investigate the memory effect of the composite electrode, the measurements were carried out in the sequence of high-to-low phosphate concentrations. The results showed that the equilibrium time values were longer than the measurement from low-to-high sequence (the inset of Fig. 5).

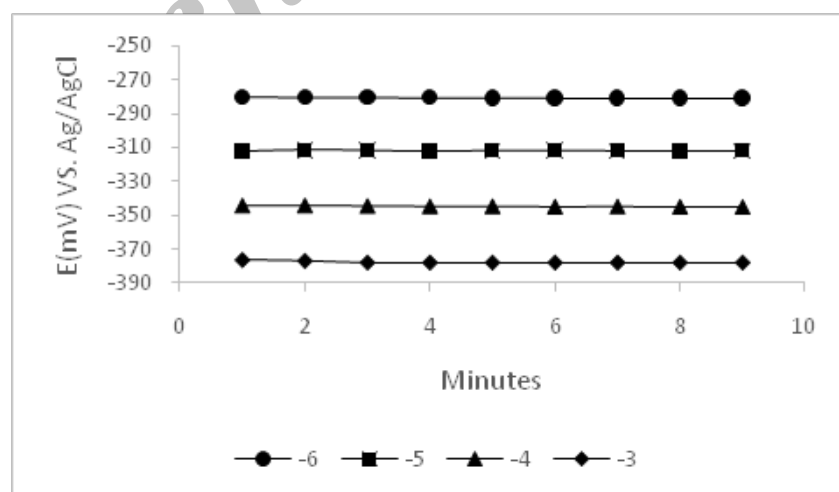


Fig. 7. Response time of the GCE-RGO-Co NPs composite electrode

3.4.3. Life time

The composite electrode showed poor response two days after fabrication. Since it had been exposed to air, the cobalt nanoparticles have been oxidized and covered by precipitates. However, storing it in deoxygenated DI water may decrease this oxidation. In order to evaluate the life time, the composite electrode was immersed in phosphate solutions (10^{-5} and 10^{-3} M) and the responses were monitored for six successive days. For lower concentration solution, the response changes were larger (Fig. 8).

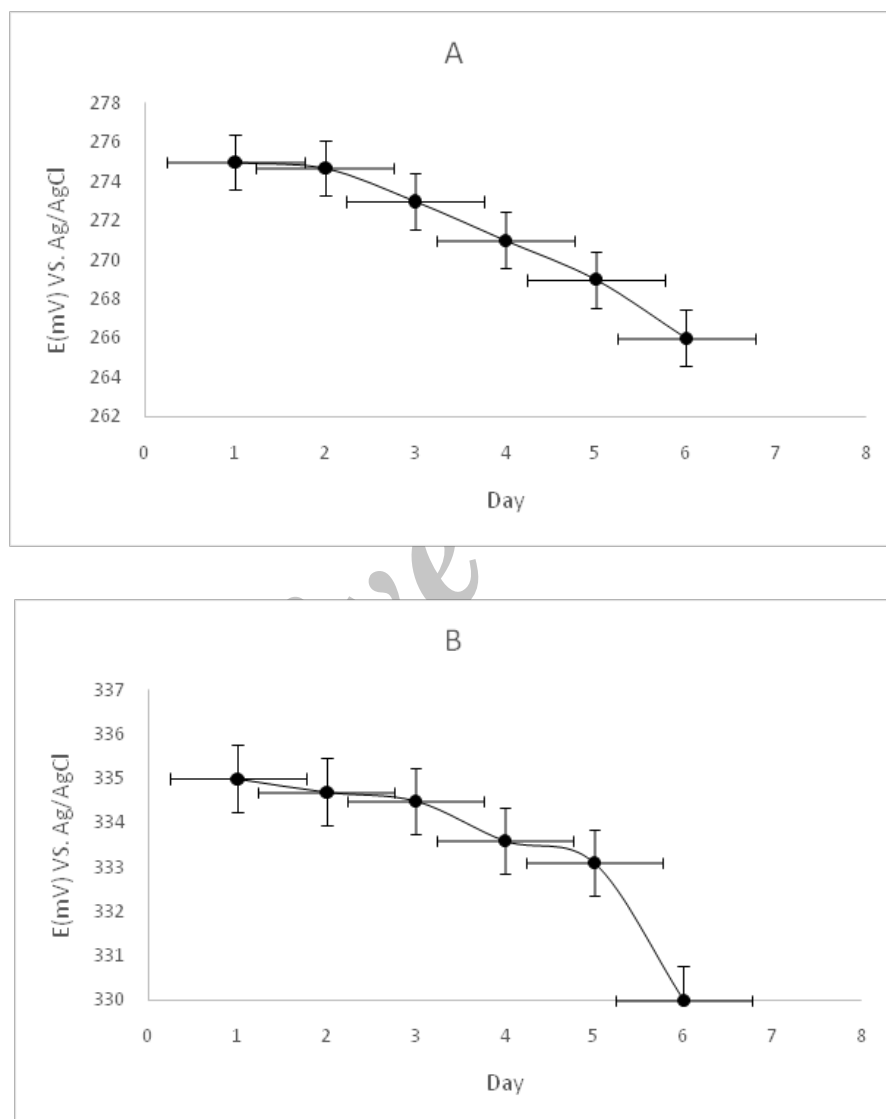


Fig. 8. Life time of the composite electrode in 10^{-3} M (A) and 10^{-5} M (B) phosphate solution

3.5. Interferences study

3.5.1. Effect of pH

The composite electrode developed here is intended to be applied in determination of phosphate in water samples. Three sets of phosphate standard solutions with pH values of 7.3, 7.8 and 8.5 were chosen for evaluation of the effect of pH on the composite electrode performance. Results shown in Fig. 9 indicated that varying pH between 7.3 and 8.5 did not show any significant effect on the electrode. However the pH of the real sample has to be considered and calibration must be carried out at the pH value of the real sample solution.

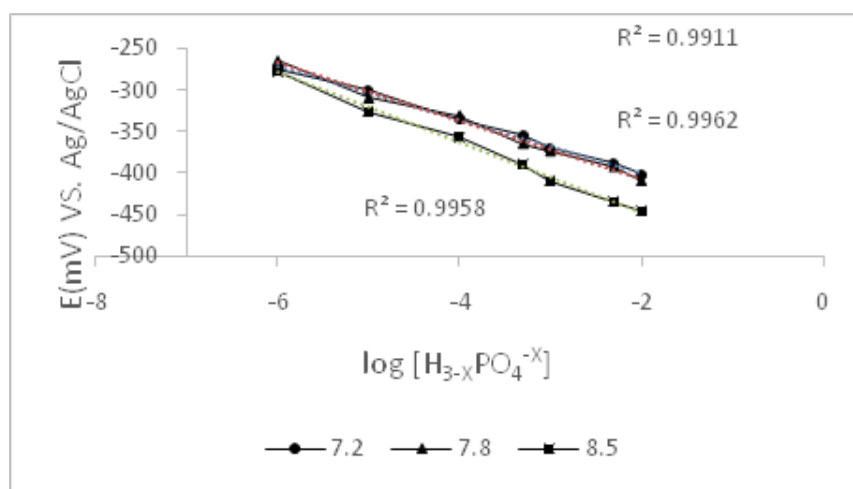


Fig. 9. effect of pH on electrode performance

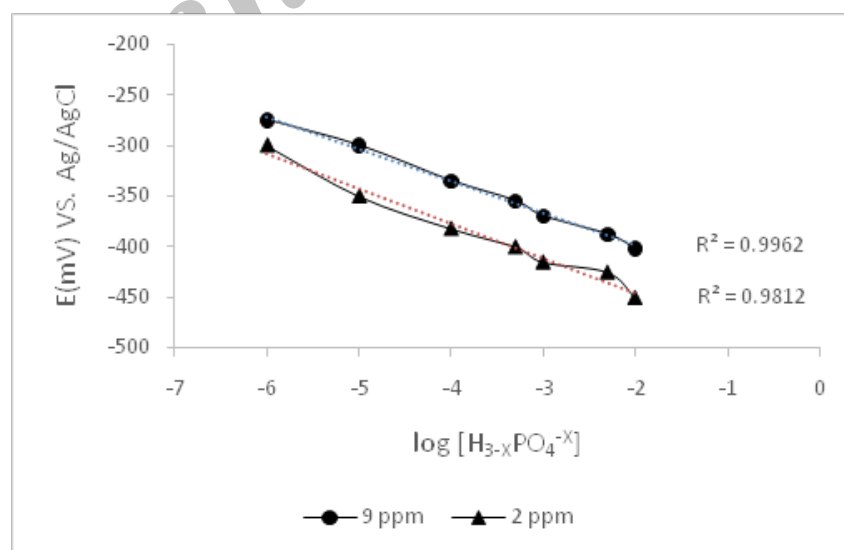


Fig. 10. effect of dissolved oxygen on the electrode performance

3.5.2. *Effect of Dissolved oxygen*

Fig. 10 shows signal response changes of the composite electrode under different dissolved oxygen concentrations.

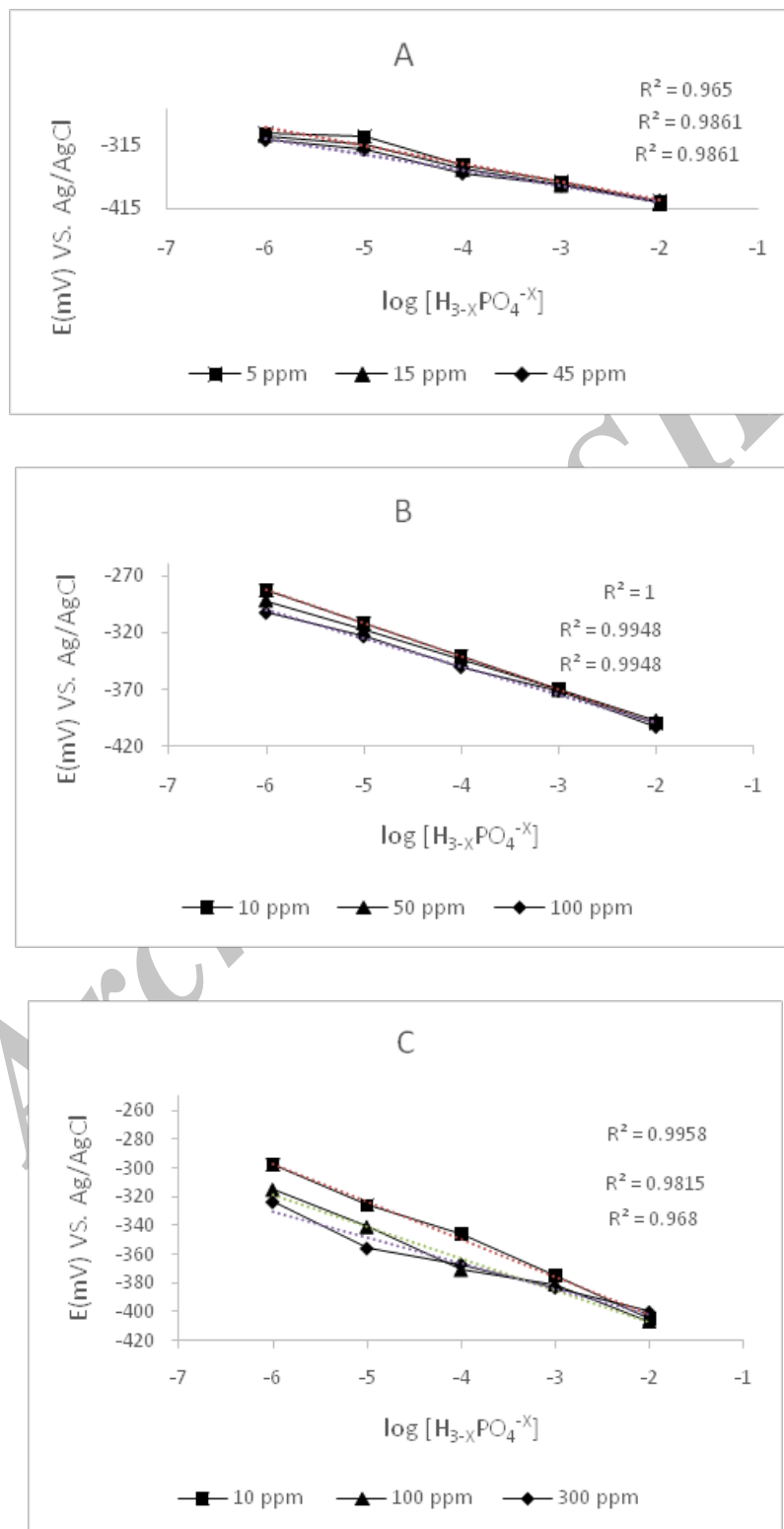


Fig. 11. Effect of (A) nitrate (B) sulfate (C) chloride interferences on electrode performance

Two set of phosphate standard solutions with 2 ppm and 8 ppm dissolved oxygen were tested to evaluate the electrode performance. It seems that oxygen interferes with the binding mechanism between cobalt nanoparticles and phosphate which results in changing the potential readings. As the dissolved oxygen decreases, the signal response of composite electrode to phosphate ion increases. However, the calibration curve still shows good sensitivity toward phosphate. As most of the water samples have dissolved oxygen in these ranges, electrode should perform correctly in real samples.

3.5.3. Ion interference

Chloride, nitrate, and sulfate ions commonly found in water samples were tested to evaluate the performance of the composite electrode. Interfering ions were kept constant, while the phosphate ion was changed from 10^{-6} to 10^{-2} M. Fig. 11 shows the ion interference tests results. All the calibration curves show a linear response towards phosphate ion and the shifts seem to be minor in the presence of interfering ions. The results showed that sensor has good selectivity towards phosphate ions and for real water samples it is possible to measure the phosphate concentrations. However for analyzing the sample solutions with higher concentration of interfering ions, concentrations of these anions need to be estimated. It is preferable to re-calibrate the composite electrode in these samples.

3.5.4. Stirring effect

To evaluate the stability of the potentiometric responses in the flowing condition, measurement was carried out while the test solution was agitated at 250 rpm. Fig. 12 shows that stirring have small effect on calibration curve and it still exhibited a good linear relationship.

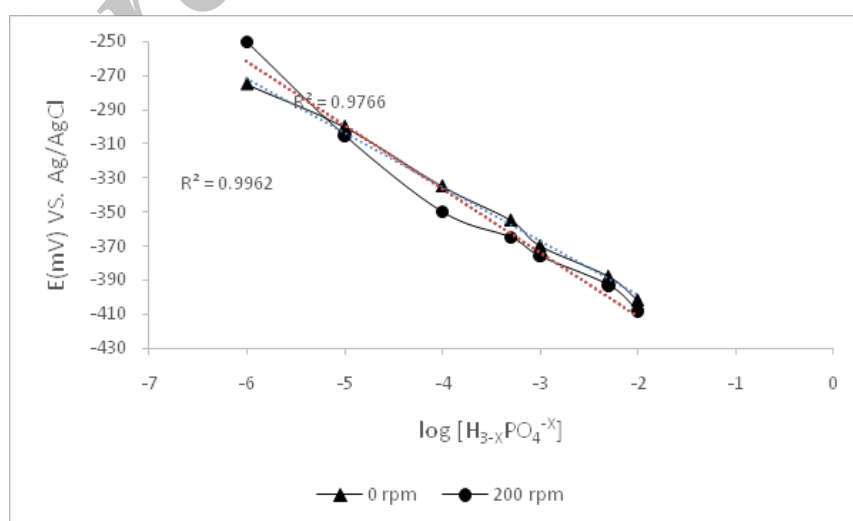


Fig. 12. Effect of stirring on electrode performance

However it should be noted that in the lower end of phosphate concentrations, the stability of potentiometric response decreases.

3.5.6. Real Samples

Cobalt-decorated graphene nanocomposite electrode was applied for phosphate sensing in real water samples. Before measurement, pH of the samples were adjusted to 7.3 (± 0.1) with sodium hydroxide. Tap and well water samples were collected from drinking water system of Tehran and Chemistry and Chemical Engineering Research Center respectively (Table 1). The relative recovery values were verified by the analysis of samples spiked with known amounts of phosphate.

Table 1. Determination of phosphate in tap and well water samples

Sample	Added Phosphate (mg L ⁻¹)	Found (mg L ⁻¹), Mean \pm SD ^a	Relative recovery (%)
Tap water	0	nd ^b	-
	5	4.93 \pm 0.03	98.6
	10	10.13 \pm 0.05	101.3
	50	52.23 \pm 0.09	104.4
well water	0	3.63 \pm 0.05	-
	5	8.58 \pm 0.07	99.0
	10	13.51 \pm 0.10	98.8
	50	48.52 \pm 0.13	97.0

^a standard deviation (n = 3).

^b Not detected.

4. CONCLUSION

An electrochemical approach to fabricate a graphene-cobalt nanoparticles composite electrode on the glassy carbon electrode was examined. Cyclic voltammetry utilized in order to deposit graphene on the glassy carbon electrode and also synthesizing cobalt nanoparticles. Scanning electron microscopy along with EDX analysis was carried out to characterize the composite electrodes. The performance of the electrode towards phosphate ion was investigated under different conditions such as pH, dissolved oxygen, ion interferences, and stirring. The potentiometric response for the range of 10⁻⁶ to 10⁻² M showed a good linear relationship with the logarithm of phosphate concentrations with a slope of -31.6 mV per decade change of concentration and R² value of 0.99. The composite electrode yielded steady potentials within 15 s varying pH between 7.3 and 8.5 did not show any significant effect on the electrode. The proposed nanocomposite electrode was applied for phosphate sensing in

tap and well water samples. Electrochemical approach has found to be a simple, cheap, and green method for fabricating the graphene-metal nanoparticles composite electrode.

REFERENCES

- [1] B. Wehrli, and R. Gacher, *Environ. Sci. Technol.* 32 (1998) 3659.
- [2] C. J. Richardson, and S. S. Qian, *Environ. Sci. Technol.* 33 (1999) 1545.
- [3] R. Kumar, *Curr. Opin. Nephrol. Hypertension* 18 (2009) 281.
- [4] E. Slatopolsky, *Kidney Int.* (2011) 34.
- [5] K. H. Chen, J. H. Liao, H. Y. Chan, and J. M. Fang, *J. Org. Chem.* 74 (2009) 895.
- [6] S. Motomizu, R. Oshima, and L. Ma, *Anal. Sci.* 13 (1997) 401.
- [7] H. Mori, H. Kogure, H. Takei, and H. Yamamoto, *Anal. Sci.* 12 (1996) 137.
- [8] A. N. Ejhieh, and N. Masoudipour, *Anal. Chim. Acta* 658 (2010) 68.
- [9] D. Xiao, H. Y. Yuan, J. Li, and R. Q. Yu, *Anal. Chem.* 67 (1995) 288.
- [10] Z. Chen, R. De Marco, and P. Alexander, *Anal. Commun.* 34 (1997) 93.
- [11] H. J. Kim, J. W. Hummel, K. A. Sudduth, and S. J. Birrell, *Trans. ASABE* 50 (2007) 415.
- [12] J. J. Wang, and P. L. Bishop, *Environ. Pollut.* 158 (2010) 3612.
- [13] J. H. Lee, W. H. Lee, P. L. Bishop, and I. Papautsky, *J. Micromech. Microeng.* 19 (2009) 25022.
- [14] R. K. Meruva, M. E. Meyerhoff, *Anal. Chem.* 68 (1996) 2022.
- [15] F. P. Ouyang, H. Zou, X. Ni, S. L. Peng, J. Ouyang, and Y. Chen, *Wuli Huaxue Xuebao/ Acta Physico-Chim. Sin.* 29 (2013) 250.
- [16] Y. Shao, J. Wang, H. Wu, J. Liu, I. Aksay, and Y. Lin, *Electroanalysis* 21 (2010) 139.
- [17] Y. Shao, J. Wang, H. Wu, J. Liu, I. A. Aksay, Y. Lin, *Electroanalysis* 22 (2010) 1027.
- [18] K. R. Ratinac, W. Yang, J. J. Gooding, P. Thordarson, and F. Braet, *Electroanalysis* 23 (2011) 803.