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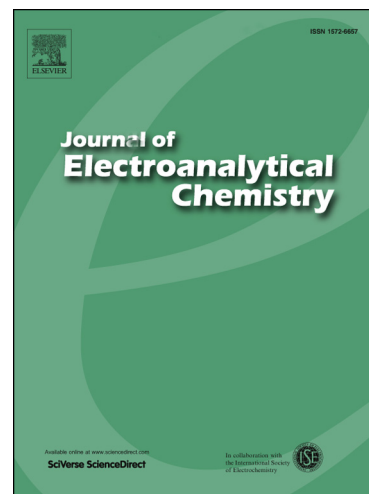
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Fabrication of carbon paste electrode containing a new inorganic-organic hybrid based on $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ polyoxoanion and Nile blue and its electrocatalytic activity toward nitrite reduction

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Abstract

In this study, a new inorganic-organic hybrid compound consisting of a Keggin type polyoxometalate, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (SiW_{12}), and Nile blue (NB) was synthesized and characterized. The $(\text{NB})_2\text{H}_2\text{SiW}_{12}\text{O}_{40}$ ($\text{NB}_2\text{SiW}_{12}$) hybrid compound was characterized by Fourier transform infrared (FT-IR), elemental (CHNS) analysis, UV-Vis and thermogravimetry techniques, and used as a bulk modifier to fabricate a chemically modified carbon paste electrode (CPE) by direct mixing. The electrochemical behavior of the newly $\text{NB}_2\text{SiW}_{12}$ composite CPE was analyzed by cyclic voltammetry, and the electrode was applied for nitrite reduction, exhibiting high electrocatalytic activity. Determination of nitrite by fixed potential amperometry was done under various experimental conditions and, at the optimum conditions, the linear response ranged from 5 to 1200 μM with a high sensitivity of and a low detection limit. The electrode has the remarkable advantage of surface renewal owing to bulk modification, as well as simple preparation, good mechanical and chemical stability and reproducibility. No noticeable interferences from other ionic species usually found in natural water were observed. The new developed electrode has been successfully applied for detection of nitrite in real water samples.

Keywords: Carbon paste electrode; Composite electrode; Inorganic-organic hybrid compound; Polyoxometalate; Nile blue; Nitrite

1. Introduction

Polyoxometalates (POMs), as metal-oxygen cluster species, are a large and rapidly growing class of compounds, that have attracted much attention in the areas of catalysis, medicine, bioanalysis and materials science, owing to their excellent properties such as the possibility of tuning POM size, shape, charge density, acidity, redox potential, stability and solubility characteristics [1, 2]. One of the most important properties of POM anions is their ability to accept various numbers of electrons, giving rise to mixed-valency species [3]. This property has made these compounds very attractive in electrode modification and electrocatalytic research [4].

A number of strategies have been developed to prepare chemically modified electrodes (CMEs) with a variety of POMs. Several groups have immobilized POMs using various techniques, such as electrochemical deposition [5-7], adsorption [8-10], use of carbon nanotubes [11], doping in a polymer matrix [12-14], layer by layer molecular self-assembly process based on electrostatic attraction as the driving force [15, 16] and entrapment in sol-gel matrix [17, 18]. One of the drawbacks of the electrodes modified by these methods is that the electrode surfaces cannot be renewed in the event of leakage, contamination or passivation, therefore it is useful to explore a novel POM-based material, that retains the electrochemical and electrocatalytic activity of POM and can be used as bulk modifiers of carbon paste electrodes, the surface of which can be renewed with very good repeatability.

Inorganic-organic hybrid POM-based materials with organic or biochemical substances have led to great achievements in the recent years, as they combine both inorganic and organic merits, possess new synergistic properties and poor solubility in water and in common organic solvent [19, 20]. Several organic compounds have been used for the synthesis of POM-based hybrid

materials [21-25]. Among them, organic dyes have a large planar conjugated π system and are excellent electron donors, offering the opportunity to be a good candidate to form POM-based charge transfer salts with a mixed valence state on the organic and inorganic units [26]. Nile blue, one of phenoxazine dyes, is a well-known electroactive molecule with highly promising properties as a redox catalyst [27]. This compound has been used as mediator for the electrocatalytic oxidation of NADH [28-30], hydrogen peroxide [31], L-cysteine [32], and nitrite [33] and electrocatalytic reduction of oxygen [34] and hemoglobin [35, 36].

In the present work, we reported the synthesis of a new inorganic-organic hybrid based on $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ polyoxoanion and Nile blue. The hybrid compound was characterized by Fourier transform infrared (FT-IR), elemental (CHNS) analysis, UV-Vis and thermogravimetry techniques and used as a solid bulk modifier to fabricate a chemically modified carbon paste electrode (CPE) by direct mixing. Electrochemical behavior of the $\text{NB}_2\text{SiW}_{12}$ modified CPE was investigated by cyclic voltammetry and applied to determine nitrite by fixed potential amperometry.

2. Experimental

2.1. Reagents and solutions

All aqueous solutions were prepared with distilled water. All chemicals were of analytical grade from Merck and Fluka and used without further purification. 1.0 M nitrite solution was prepared by dissolving sodium nitrite in water. 1.0 M H_2SO_4 solution was prepared in water and different pH solutions were prepared by adjusting the pH with required amount of 1.0 M NaOH solution.

Samples of natural water were taken from Zayandeh road river, Isfahan, Iran.

2.2. Apparatus

A Leco CHNS-932 elemental analyzer was utilized for the structure characterization of hybrid compound. FT-IR spectrum was recorded in the 400-4000 cm^{-1} range on a JASCO model FT-IR-3600 spectrometer using KBr pellets. Solid state diffuse reflectance spectra between 200 and 800 nm were obtained for the dry pressed disk samples using a JASCO model V-670 spectrophotometer. UV-Vis spectra in organic solvent were measured on a Shimadzu UV 160 spectrometer using spectrophotometric grade dimethylsulfoxide (DMSO) as solvent. Thermogravimetric analyses were carried out between 25 and 750 $^{\circ}\text{C}$ in dynamic air atmosphere at $10^{\circ}\text{C min}^{-1}$ on Mettler TA4000/TG-50 thermobalance.

An Autolab electrochemical analyzer model PGSTAT30 (Eco Chemie, Utrecht, The Netherlands) controlled by a microcomputer with GPES 4.9 software was used for voltammetric measurement. A three-electrode cell was used, including carbon paste electrode or $\text{NB}_2\text{SiW}_{12}$ composite carbon paste electrode as working electrode, together with an Ag/AgCl (saturated KCl) and a platinum wire as reference and counter electrode, respectively.

The pHs of solutions were measured by a Metrohm model 827 pH meter using a combined glass electrode (Metrohm 6.0262.100).

2.3. Synthesis of $\text{NB}_2\text{SiW}_{12}$

The NB solution containing 0.4 mM NB in 0.1 M HCl was dropped, at room temperature, to an aqueous solution containing 0.1 mM SiW_{12} , under vigorous stirring. After 30 min stirring, the dark blue precipitate formed was filtered and washed with water to remove all unreacted NB and dried at 120°C for 5 h. CHNS analysis Calcd. (found): C: 13.98 (14.04), H: 1.48 (1.54), N: 2.31 (2.27) and FT-IR (KBr, cm^{-1}): 2963, 2872 ($\nu_{\text{C-H}}$), 1643 ($\nu_{\text{C=N}}$), 1328, 1470, 1585 ($\nu_{\text{C=C}}$), 1134

(v_{C-N}), 1013 (v_{Si-Oa}), 971 (v_{W-Od}), 921 (v_{W-Ob-W}), 793 (v_{W-Oc-W}) confirm the synthesis of NB_2SiW_{12} .

2.4. Fabrication of the carbon paste electrodes

The unmodified carbon paste electrode was prepared by mixing graphite powder with an appropriate amount of paraffin oil (70:30 w/w). A portion of the composite mixture was packed into a 2 mm diameter insulin syringe. Electrical contact was made by forcing a copper pin down into the syringe and into the back of the graphite paste. The surface of electrode was smoothed on a piece of weighing paper.

The NB_2SiW_{12} composite electrode was prepared by mixing the graphite paste with NB_2SiW_{12} (85:15 w/w). In order to obtain a better homogeneity and good reproducibility of the composite electrode surface, ethanol was added to the resulted composite. The mixture was stirred using a magnetic stirrer until all the solvent evaporated. The composite was then air dried for 24 h and the composite electrode was fabricated in the same way as graphite one.

3. Result and discussion

3.1. Characterization of NB_2SiW_{12}

3.1.1 CHN elemental analysis and thermogravimetry.

The percentage of C and N determined by elemental analysis of NB_2SiW_{12} was found to be 14.0 and 2.3%, respectively, corresponding to the reaction of 2 NB moles with one mole of SiW_{12} to form NB_2SiW_{12} . Thermogravimetric data showed a 4.30% weight loss below 200°C, corresponding to the release of hydrated water. At temperatures higher than 597°C, the hybrid compound being slowly decomposed to the final products SiO_2 and WO_3 [37]. The relative lost

weight of organic part to total weight shows that one mole of SiW_{12} reacted with 2 moles of NB cations to form $\text{NB}_2\text{SiW}_{12}$ hybrid compound, which confirms the CHN.

3.1.2. UV-Vis spectra

The diffuse reflectance (DR) UV-Vis spectra of SiW_{12} exhibited two strong bands at 254 and 329 nm and of NB showed other less strong bands at 392 and 459 nm and broad strong absorption band from 500 to 800 nm. Hybrid compound exhibited also the adsorption bands of the components NB and SiW_{12} and a new band at 524 nm (Fig. 1A), attributed to the charge transfer transitions between the SiW_{12} acceptor and NB donor [38, 39]. The UV-Vis spectra in DMSO solution of SiW_{12} , NB and hybrid (see Fig. 1B) showed that SiW_{12} has a high intensity absorption peak at 288 nm, attributed to the O-W charge transfer transitions [40] and that NB possesses absorption bands at 638 and 275 nm. The hybrid compound UV-Vis spectra exhibited all the absorption bands of both SiW_{12} and NB, with hypsochromic shifts of the NB peaks due to the interaction between SiW_{12} and NB in the hybrid compound.

<Figure 1>

3.2. Electrochemical properties of modified electrode

As known, POM compounds are unstable in neutral and basic aqueous solutions and undergo a series of hydrolysis processes, but they are fairly stable in acidic aqueous solutions [41]. Therefore, electrochemical studies of the $\text{NB}_2\text{SiW}_{12}$ composite electrode were carried out in 1.0 M H_2SO_4 aqueous solutions, pH 1.0. As shown in Fig. 2 (a) cyclic voltammetry of the $\text{NB}_2\text{SiW}_{12}$ composite electrode in the potential range from -0.8 V to +0.6 vs Ag/AgCl shows three pairs of reversible redox peaks with the half wave potentials ($E_{1/2} = (E_{pa} + E_{pc})/2$) of -0.25 (II-II'), -0.49 (III-III') and -0.72 (IV-IV') V vs. Ag/AgCl, that correspond to the reduction and oxidation of

one, one and two electron processes of tungsten center in SiW_{12} part, respectively [37]. The formal potentials $E_{1/2}$ of SiW_{12} in the hybrid compound are shifted towards more negative potentials compared to the SiW_{12} alone (see Fig. 2b), when their values are -0.19 (II-II'), -0.44 (III-III') and -0.70 (IV-IV') V vs. Ag/AgCl. This indicates that SiW_{12} acts as an electron acceptor in hybrid compound, and since the electron density of SiW_{12} increases in the hybrid compound, a higher potential is needed for its reduction than in SiW_{12} anion.

The main redox activity of NB is observed at potentials very close to 0.0 V vs. Ag/AgCl, presenting reversible peaks with $E_{1/2} +0.06$ V vs. Ag/AgCl, a less evident pair of peaks, with $E_{1/2} = +0.37$ V, being also noticeable (see Fig 2,c). In the $\text{NB}_2\text{SiW}_{12}$ hybrid compound, the main redox activity is maintained, the redox process being irreversible and the oxidation wave occurring at a potential closer to 0.0 V, indicating that NB is oxidized easier in the hybrid compound, due to the electron acceptor nature of SiW_{12} .

<Figure 2>

3.2.1. Effect of pH and scan rate

In general, the reduction of POM anions is accompanied by protonation, therefore, the pH of the supporting electrolyte, is expected to have an effect on the electrochemical behavior of the $\text{NB}_2\text{SiW}_{12}$ composite CPE. Fig. 3A exhibits the CV-s recorded in six different pH solutions, from 0.5 to 2.0, obtained by mixing 1.0 M H_2SO_4 with 1.0 M NaOH, and showing clearly the effect of pH on the redox peaks potentials characteristic of POM in the hybrid compound (peaks II, III and IV). As seen in Fig. 3B, an increase of pH from 0.5 to 2 leads to linear decrease of the potentials values.

<Figure 3>

Fig. 4 represents the CVs of the $\text{NB}_2\text{SiW}_{12}$ composite CPE at scan rates from 10 to 100 mV s^{-1} in the potential range +0.6 to -0.8 V vs. Ag/AgCl in H_2SO_4 pH 1.0 solution. As observed from Fig 4, inset, the peak currents of all redox pairs increased linearly with the scan rate, suggesting that the redox process is surface-confined. The peak-to-peak potential separation for the redox peak pairs is about 50 mV, larger than the theoretical value, which should be 0 mV for a reversible surface redox process [42].

<Figure 4>

3.2.2. Stability and repeatability of surface-renewal

The working stability of the $\text{NB}_2\text{SiW}_{12}$ composite CPE was investigated by recording repetitive cyclic voltammograms and monitoring the change in peak current density and peak potentials. The electrode retained 99% of its initial activity after 100 repetitive cycles in 1.0 M H_2SO_4 pH 1.0 in the potential range of +0.6 to -0.8 V vs. Ag/AgCl. High stability of the $\text{NB}_2\text{SiW}_{12}$ composite CPE could be related to the strong electrostatic attraction between NBCl and POM and insolubility of the hybrid compound in water.

The composite electrode also showed excellent long term stability. The electrode was tested during 1 month, 5 times per week, by recording 10 CV-s in H_2SO_4 (pH 1.0) solution. Its initial peak current intensities decreased only slightly (with $\approx 8\%$) after 1 month of use.

One of the main advantages of bulk modified electrodes over surface modified electrodes is that the electrode surface can be renewed easily. The reproducibility of the electrode surface was studied by renewing the modified electrode surface seven times and recording a CV scan after each, in 1.0 M H_2SO_4 pH 1.0. Data obtained showed an excellent R.S.D of 3.8%.

These results are very promising for analytical application of the newly developed electrode.

3.3. Electrocatalytic activity NB_2SiW_{12} composite CPE towards nitrite

Many studies [4, 12, 43-47] have shown that reduced POMs are capable of delivering electrons to important analytical species, thus serving as powerful electron reservoirs for multi-electron reductions. In this work, we evaluate the applicability of the NB_2SiW_{12} composite CPE for the electrocatalytic reduction of nitrite.

3.3.1. Electrocatalytic reduction of nitrite at NB_2SiW_{12} composite CPE

Cyclic voltammograms were recorded at bare CPE and NB_2SiW_{12} composite CPE in 1.0 M H_2SO_4 (pH 1.0) solutions containing different concentrations of nitrite. As shown in Fig. 5, the electroreduction of nitrite on the bare CPE requires a large overpotential of ≈ 0.8 V vs. Ag/AgCl, which is significantly lowered at NB_2SiW_{12} composite CPE, due to its electrocatalytic activity towards nitrite reduction. By increasing the concentration of nitrite, the cathodic current increases while the oxidation one decreases at potentials higher than -0.2 V vs. Ag/AgCl, required for nitrite electrocatalysis.

<Figure 5>

3.3.2. Amperometric detection of nitrite at NB_2SiW_{12} composite CPE

Since the cyclic voltammetry is not particularly sensitive to low concentrations of analyte, the fixed potential amperometry was used to fully evaluate the sensor analytical properties. The influence of the applied potential on the response of NB_2SiW_{12} composite CPE to nitrite was tested between -0.1 to -0.35 V vs. Ag/AgCl and, as expected, the sensor response is higher at more negative potentials. Nevertheless, at -0.25 V vs Ag/AgCl the sensor response was high enough, and was chose for further experiments in order to reduce the effect of other interfering ions, such as BrO_3^- , ClO_3^- , IO_3^- potentially present in samples together with nitrite.

Fig 6A displays the typical hydrodynamic amperometric response of the $\text{NB}_2\text{SiW}_{12}$ modified CPE (rotation speed 2000 rpm) during successively addition of nitrite in 1.0 M H_2SO_4 pH 1.0. The time required to reach the 95% steady-state response was 5s, indicating a fast response process. The amperometric response to nitrite showed a linear range from 5 to 1200 μM (Fig. 6B), with the calculated detection limit of $2.8 \pm 0.42 \mu\text{M}$ (RSD = 3.9%, $n=3$). The sensitivity of the amperometric nitrite sensor was $178.2 \pm 2.1 \mu\text{A mM}^{-1} \text{cm}^{-2}$ (RSD = 4.7%, $n=3$).

A comparison of the analytical properties of recently reported nitrite sensors are listed in Table 1. The detection limit of the $\text{NB}_2\text{SiW}_{12}$ modified CPE was lower than most other electrodes, the linear range being similar to the other reported electrodes, the $\text{NB}_2\text{SiW}_{12}$ composite CPE having the advantage in being very easy to prepare from cheap materials compared to other more complex electrode architecture cited in the Table 1.

<Figure 6>

<Table 1>

3.3.3. Interference study

The influence of various ions which often exist in the nitrite containing samples, such as BrO_3^- , ClO_3^- , ClO_4^- , CO_3^{2-} , HCO_3^- , NO_3^- , F^- , Cl^- , I^- , Br^- , H_2O_2 , IO_3^- , Na^+ , Mg^{2+} and Ca^{2+} , on the determination of nitrite was studied. The amperometric response of the sensor to nitrite in the presence of interferents was tested for the concentration ratio of 10:1 interefrent:nitrite. The results are summarized in Table 2 showing that sensor is almost interferent-free. Only I^- , Br^- and IO_3^- interfere in the nitrite determination, which should not be a problem in real samples nitrite determination, where their concentration in relation to nitrite is much lower than 10:1, here tested. The catalytic selectivity is enhanced by the low working potential (-0.25 V vs. Ag/AgCl),

which in combination with the great operational stability, makes the proposed sensor a promising tool to be used for nitrite in real samples with no, or minimal sample preparation.

<Table 2>

3.3.4. Application of the sensor

The $\text{NB}_2\text{SiW}_{12}$ modified CPE was used to determine nitrite in natural water from Isfahan, Iran (Zayandehrood river). A volume of 1 ml of water was injected into a 20 mL electrochemical cell, followed by injection of nitrite standard solution corresponding to 50, 100 and 150 μM nitrite in the total cell volume. The nitrite concentrations in the water sample and after the additions of standard solution of nitrite were determined from interpolation on the calibration curve recorded right before the experiment. Results are presented in Table 3. As observed, the recoveries were very close to 100 % (98.7-101.6%), indicating that the developed amperometric nitrite sensor can be successfully applied to the analysis of nitrite in water samples.

<Table 3>

4. Conclusions

In this study, an inorganic-organic polyoxometalate (SiW_{12}) - Nile Blue (NB) hybrid was synthesized and characterized by different techniques. Thermogravimetric and CHNS studies showed that 2 moles of NB react with one of SiW_{12} to form $\text{NB}_2\text{SiW}_{12}$ hybrid compound. The UV-Vis spectra of the hybrid contained the peaks of both components, a new peak at 524 nm being attributed to the charge transfer transitions between the SiW_{12} acceptor and NB donor. The $\text{NB}_2\text{SiW}_{12}$ was introduced as a bulk modifier in a CPE, to form $\text{NB}_2\text{SiW}_{12}$ composite CPE. The CV studies showed that POM acts as an electron acceptor in $\text{NB}_2\text{SiW}_{12}$, SiW_{12} being more difficult to be oxidized in the hybrid compound, while NB oxidizes at less positive potentials

close to 0.0 V vs Ag/AgCl. The electrode exhibited a great stability and reproducibility of surface renewal, and exhibits electrocatalytic activity towards nitrite reduction, decreasing substantially the high nitrite reduction potential at unmodified CPE. Fixed potential amperometry was used successfully to determine nitrite at -0.25 V vs Ag/AgCl, the sensor having a very low detection limit of $2.8 \pm 0.42 \mu\text{M}$ (RSD = 3.9%, $n=3$) and a high sensitivity of $178.2 \mu\text{A mM}^{-1} \text{cm}^{-2}$ (RSD = 4.7%, $n=3$). Almost interference free detection of nitrite, together with very good recovery results, close to 100%, obtained for nitrite detection in water sample, make this newly developed $\text{NB}_2\text{SiW}_{12}$ composite CPE an appropriate analytical tool for nitrite detection in real samples.

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References

- [1] M. Zhu, J. Peng, H.-J. Pang, P.-P. Zhang, Y. Chen, D.-D. Wang, M.-G. Liu, Y.-H. Wang, J. Solid State Chem. 184 (2011) 1070-1078.
- [2] D.-D. Wang, J. Peng, H.-J. Pang, P.-P. Zhang, X. Wang, M. Zhu, Y. Chen, M.-G. Liu, C.-I. Meng, Inorg. Chim. Acta 379 (2011) 90-94.
- [3] M. Sadakane, E. Steckhan, Chem. Rev. 98 (1998) 219-237.
- [4] H. Hamidi, E. Shams, B. Yadollahi, F.K. Esfahani, Talanta 74 (2008) 909-914.
- [5] D.M. Fernandes, S.M.N. Simões, H.M. Carapuça, A.M.V. Cavaleiro, Electrochim. Acta 53 (2008) 6580-6588.
- [6] Y. Li, W. Bu, L. Wu, C. Sun, Sens. Actuators B 107 (2005) 921-928.
- [7] Z.Y. Tang, S.Q. Liu, E.K. Wang, S.J. Dong, E.B. Wang, Langmuir 16 (2000) 5806-5813.
- [8] D. Martel, A. Kuhn, Electrochim. Acta 45 (2000) 1829-1836.
- [9] A. Kahn, F.C. Anson, Langmuir 12 (1996) 5481-5488.
- [10] B. Wang, S. Dong, Electrochim. Acta 41 (1996) 895-916.
- [11] B. Haghghi, H. Hamidi, L. Gorton, Electrochim. Acta 55 (2010) 4750-4757.
- [12] D.M. Fernandes, C.M.A. Brett, A.M.V. Cavaleiro, J. Electroanal. Chem. 660 (2011) 50-56.
- [13] S.-M. Chen, Y.-H. Fa, J. Electroanal. Chem. 567 (2004) 9-17.
- [14] X. Zou, Y. Shen, Z. Peng, L. Zhang, L. Bi, Y. Wang, S. Dong, J. Electroanal. Chem. 566 (2004) 63-71.
- [15] M. Carcía, K. Carfumán, C. Diaz, C. Garrido, I. Osorio-Román, M.J. Aguirre, M., Electrochim. Acta 80 (2012) 390-398.
- [16] K. Jiang, H. Zhang, C. Shannon, W. Zhan, Langmuir 24 (2008) 3584-3589.
- [17] P. Wang, X. Wang, G. Zhu, Electrochim. Acta 46 (2000) 637-641.
- [18] W. Song, Y. Liu, N. Lu, H. Xu, C. Sun, Electrochim. Acta 45 (2000) 1639-1644.
- [19] X. Wang, Z. Kang, E. Wang, C. Hu, J. Electroanal. Chem. 523 (2003) 142-149.
- [20] H. Ma, J. Peng, Z. Han, X. Yu, B. Dong, J. Solid State Chem. 178 (2005) 3735-3739.
- [21] X. Wang, Q. Zhang, Z. Han, E. Wang, Y. Guo, C. Hu, J. Electroanal. Chem. 563 (2004) 221-227.
- [22] B. Dong, J. Peng, A. Tian, J. Sha, L. Li, H. Liu, Electrochim. Acta 52 (2007) 3804-3812.
- [23] C. Li, R. Cao, K.P. O'Halloran, H. Ma, L. Wu, Electrochim. Acta 54 (2008) 484-489.

- [24] M. Ammam, E. Bradley Easton, *Electrochim. Acta* 56 (2011) 2847-2855.
- [25] X. Wang, H. Hu, B. Chen, H. Lin, A. Tian, J. Li, *Solid State Science* 13 (2011) 344-349.
- [26] G. Xue, J. Xiong, H. Guo, G. Cao, S. Nie, H. Hu, *Electrochim. Acta* 69 (2012) 315-319.
- [27] Z.-W. Chen, A. Balamurugan, S.-M. Chen, *Bioelectrochem.* 75 (2009) 13-18.
- [28] P. Du, P. Wu, C. Cai, *J. Electroanal. Chem.* 624 (2008) 21-26.
- [29] L. Zhu, R. Yang, X. Jiang, D. Yang, *Electrochem. Commun.* 11 (2009) 530-533.
- [30] P. Du, S. Liu, P. Wu, C. Cai, *Electrochim. Acta* 53 (2007) 1811-1823.
- [31] P. Du, B. Zhou, C. Cai, *J. Electroanal. Chem.* 614 (2008) 149-156.
- [32] A.A. Ensafi, S. Behyan, *Sens. Actuators B* 122 (2007) 282-288.
- [33] X. Chen, F. Wang, Z. Chen, *Anal. Chim. Acta* 623 (2008) 213-220.
- [34] H.X. Ju, C. Shen, *Electroanalysis* 13 (2001) 789-793.
- [35] D.M. Zhou, H.Y. Chen, *Electroanalysis* 9 (1997) 399-402.
- [36] H. Kuramitz, K. Sugawara, M. Kawasaki, K. Hasebe, H. Nakamura, S. Tanaka, *Anal. Sci.* 15 (1999) 589-592.
- [37] F.-Y. Cui, X.-Y. Ma, C. Li, T. Dong, Y.-Z. Gao, Z.-G. Han, Y.-N. Chi, C.-W. Hu, *J. Solid State Chem.* 183 (2010) 2925-2931.
- [38] R.S. Mulliken, *J. Am. Chem. Soc.* 72 (1950) 600-608.
- [39] R. Foster, in: *Organic charge-transfer complexes*, Academic, New York, 1969.
- [40] J.W. Zhao, Y.P. Song, P.T. Ma, J.P. Wang, J.Y. Niu, *J. Solid State Chem.* 182 (2009) 1798-1805.
- [41] Z. Han, Y. Zhao, J. Peng, A. Tian, Y. Feng, Q. Liu, *J. Solid State Chem.* 178 (2005) 1386-1394.
- [42] A.P. Brown, F.C. Anson, *Anal. Chem.* 49 (1977) 1589-1595.
- [43] H. Ma, Z. Zhang, H. Pang, S. Li, Y. Chen, W. Zhang, *Electrochim. Acta* 69 (2012) 379-383.
- [44] L. Wang, Z.-G. Feng, H.-N. Cai, *J. Electroanal. Chem.* 636 (2009) 36-39.
- [45] H. Hamidi, E. Shams, B. Yadollahi, F.K. Esfahani, *Electrochim. Acta* 54 (2009) 3495-3500.
- [46] B. Haghghi, H. Hamidi, *Electroanalysis* 21 (2009) 1057-1065.
- [47] B.-Q. Huang, I. Wang, K. Shi, Z.-X. Xie, L.-S. Zheng, *J. Electroanal. Chem.* 615 (2008) 19-24.
- [48] G. Zhao, K. Liu, S. Lin, J. Liang, X. Guo, Z. Zhang, *Microchim. Acta* 144 (2004) 75-80.
- [49] H. Wang, Y. Huang, Z. Tan, X. Hu, *Anal. Chim. Acta* 526 (2004) 13-17.

- [50] Y. Tian, J. Wang, Z. Wang, *Synth. Met.* 143 (2004) 309-313.
- [51] J.X. Zeng, W.Z. Wei, X. Zhai, P. Yang, J. Yin, L. Wu, X. Liu, K. Liu, S. Gong, *Microchim. Acta* 155 (2006) 379-386.
- [52] J. Li, X. Lin, *Microchem. J.* 87 (2007) 41-46.
- [53] A. Salimi, A. Noorbakhsh, M. Ghadermarzi, *Sens Actuators B* 123 (2007) 530-537.
- [54] S. Yang, X. Zeng, X. Liu, W. Wei, S. Luo, Y. Liu, *J. Electroanal. Chem.* 639 (2010) 181-186.
- [55] P. Dreyse, M. Isaacs, K. Calfumán, C. Cáceres, A. Aliga, M.J. Aguirre, D. Villagra, *Electrochim. Acta* 56 (2011) 5230-5237.
- [56] C. Deng, J. Chen, Z. Nie, M. Yang, S. Si, *Thin Solid Films* 520 (2012) 7026-7029.

Figure Captions:

Figure 1. A) Diffuse reflectance UV-Vis spectra and B) UV-Vis spectra in 10 μM DMSO of (a) SiW_{12} , (b) NBCl and (c) $\text{NB}_2\text{SiW}_{12}$

Figure 2. Cyclic voltammograms recorded at (a) $\text{NB}_2\text{SiW}_{12}$, (b) SiW_{12} and (c) NBCl composite CPE in 1.0 M H_2SO_4 pH 1.0 solution; scan rate 100 mV s^{-1} .

Figure 3. (A) Cyclic voltammograms recorded at $\text{NB}_2\text{SiW}_{12}$ composite CPE in 1.0 M H_2SO_4 solution at different pH-s of 0.5, 0.75, 1.0, 1.5 and 2.0, scan rate 100 mVs^{-1} and (B) the linear dependence of peak potential with the pH.

Figure 4. Cyclic voltammograms recorded at $\text{NB}_2\text{SiW}_{12}$ composite CPE in 1.0 M H_2SO_4 pH 1.0 at different scan rates from 10 to 100 mV s^{-1} ; inset: the corresponding plots of peak current vs. scan rate.

Figure 5. Cyclic voltammograms recorded at bare CPE and $\text{NB}_2\text{SiW}_{12}$ composite CPE in 1.0 M H_2SO_4 pH 1.0 solution for 0.0, 0.1, 0.5 and 1.0 mM nitrite; inset are CV at bare CPE in the absence and addition of 0.1 mM nitrite; scan rate 50 mV s^{-1}

Figure 6. (A) Fixed potential amperogram recorded at $\text{NB}_2\text{SiW}_{12}$ composite CPE for successive additions of nitrite in 1.0 M H_2SO_4 pH 1.0 solution at -0.25 V vs. Ag/AgCl , 2000 rpm and (B) corresponding calibration curve.

Table 1. Comparison of some chemically modified electrodes for electroreduction of nitrite.

Electrode	Linear range	LOD (μM)	Applied potential (V) vs. Ag/AgCl	Reference
CNTs/GCE ^a in the presence of Cu ions	2-10 μM and 20 μM -1 mM	0.5	-0.55	48
Cu Nps ^b thin-films electrode	50 μM -30 mM	20.0	-0.30	49
Polypyrrole nanowires/GCE	22.8 μM -20 mM	22.8	0.18	50
CNTs/PAA/GCE	3 μM -4.5 mM	1.0	0.10	51
Polypyrrole/Pt/GCE	0.5 μM -1 mM	0.2	-0.12	52
Catalase/CNTs/GCE	5 μM -10 mM	1.4	0.30	53
Cu Nps/CNTs/GCE	1 μM -0.6 mM	0.1	-0.05	54
Poly-NiTRP ^c -GCE	14.9-124 μM	9.4	-0.80	55
PTH ^d /CNTs/GCE	0-50 mM	1.4	0.30	56
NB ₂ SiW ₁₂ composite CPE ^e	5-1200 μM	2.8	-0.25	This work

^aCarbon Nano Tubes Glassy Carbon Electrode

^bNanoparticles

^cpoly-[Ni(S-NO₂-phen)₂Cl]tetra pyridyl porphyrin

^dpolythionine

^eCarbon Paste Electrode

Table 2. Effect of interfering species on the amperometric determination of nitrite with NB₂SiW₁₂ composite CPE.

Interferents	Current ratio ^a
BrO ₃ ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , CO ₃ ²⁻ , HCO ₃ ⁻ , NO ₃ ⁻ , F ⁻ , Cl ⁻ , H ₂ O ₂ , Na ⁺ , Mg ²⁺ , Ca ²⁺	1.0
Br ⁻	1.5
I ⁻	1.8
IO ₃ ⁻	2.1

^a current ratio was obtained by comparing the current response of 0.1 mM nitrite + 1.0 mM interfering species with 0.1 mM nitrite.

Table 3. Analytical results of the amperometric nitrite sensor for water taken from Zayandehrood river, Isfahan, Iran

Sample	Nitrite added (μM)	Nitrite found (μA) (n=4) ^a	Recovery (%)
water	-	$15.55 \pm 4.15^{\text{b}}$	-
Mixture 1	50	66.62 ± 4.26	101.6 ± 6.5
Mixture 2	100	114.05 ± 3.53	98.7 ± 3.1
Mixture 3	150	164.21 ± 3.83	99.2 ± 2.3

^a Average of four determinations \pm relative standard deviation.

^b Nitrite concentration found in the river water

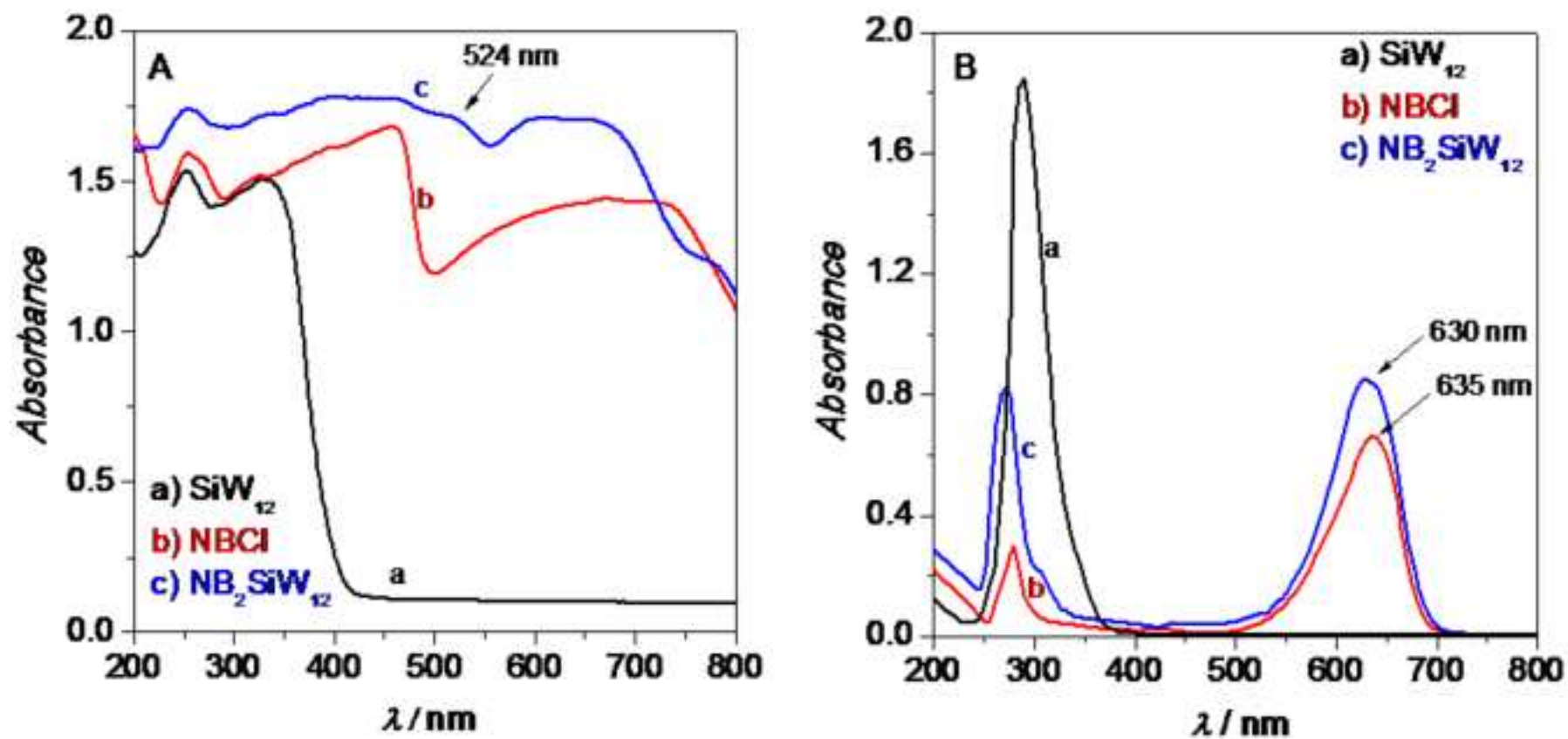


Figure 1

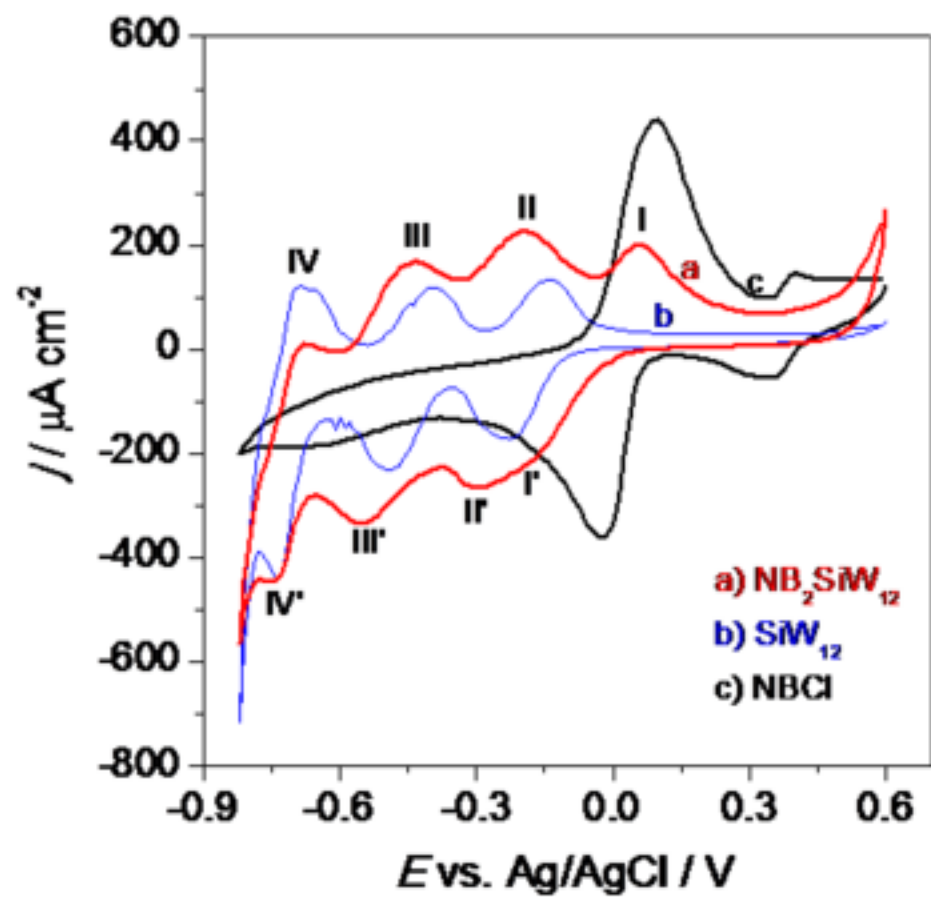


Figure 2

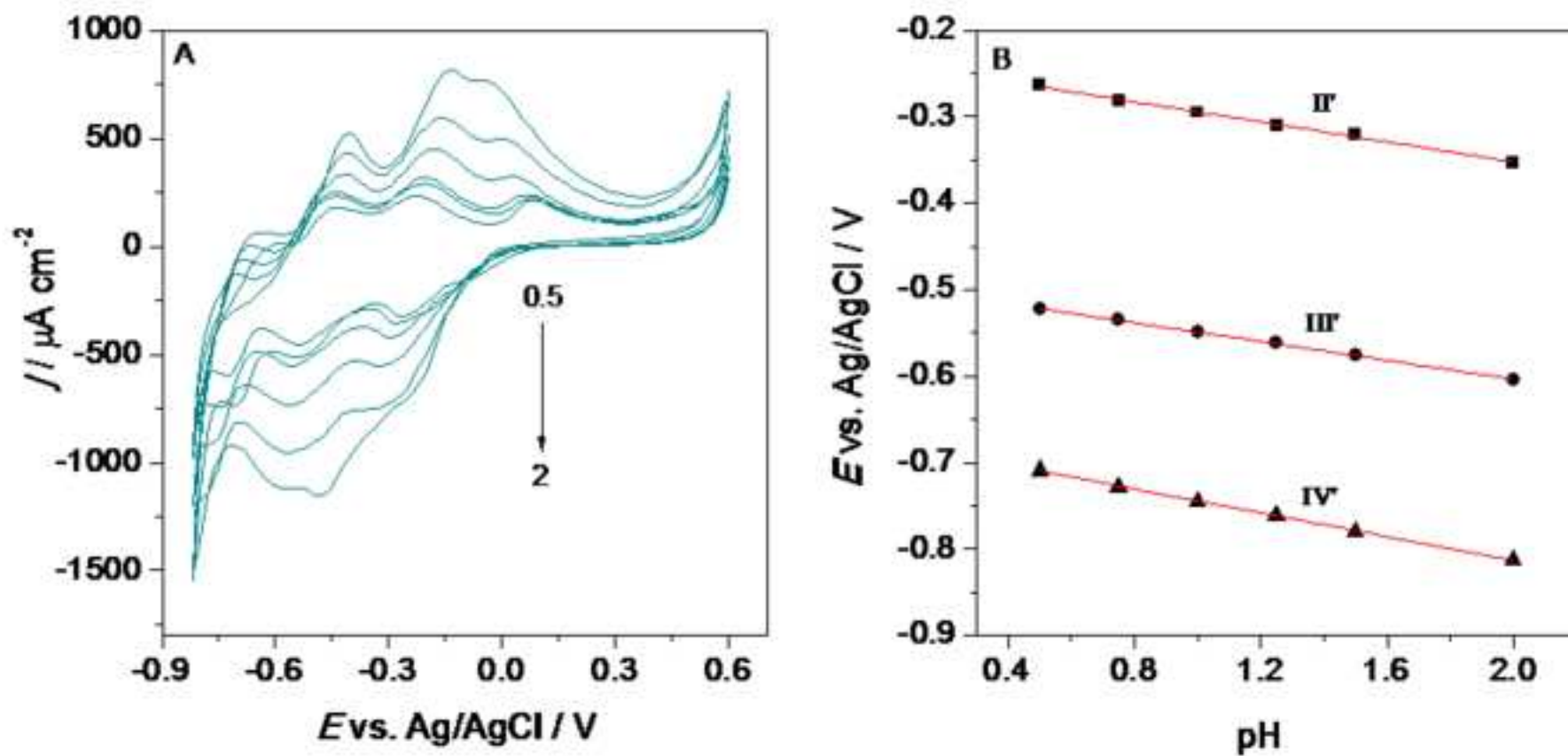


Figure 3

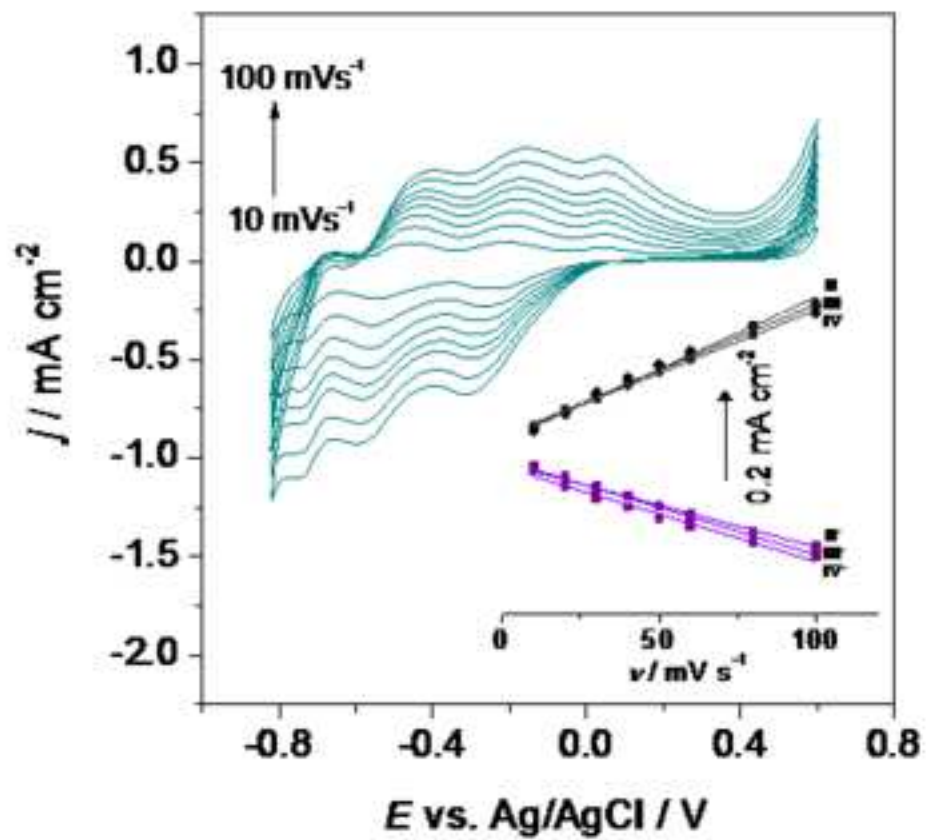


Figure 4

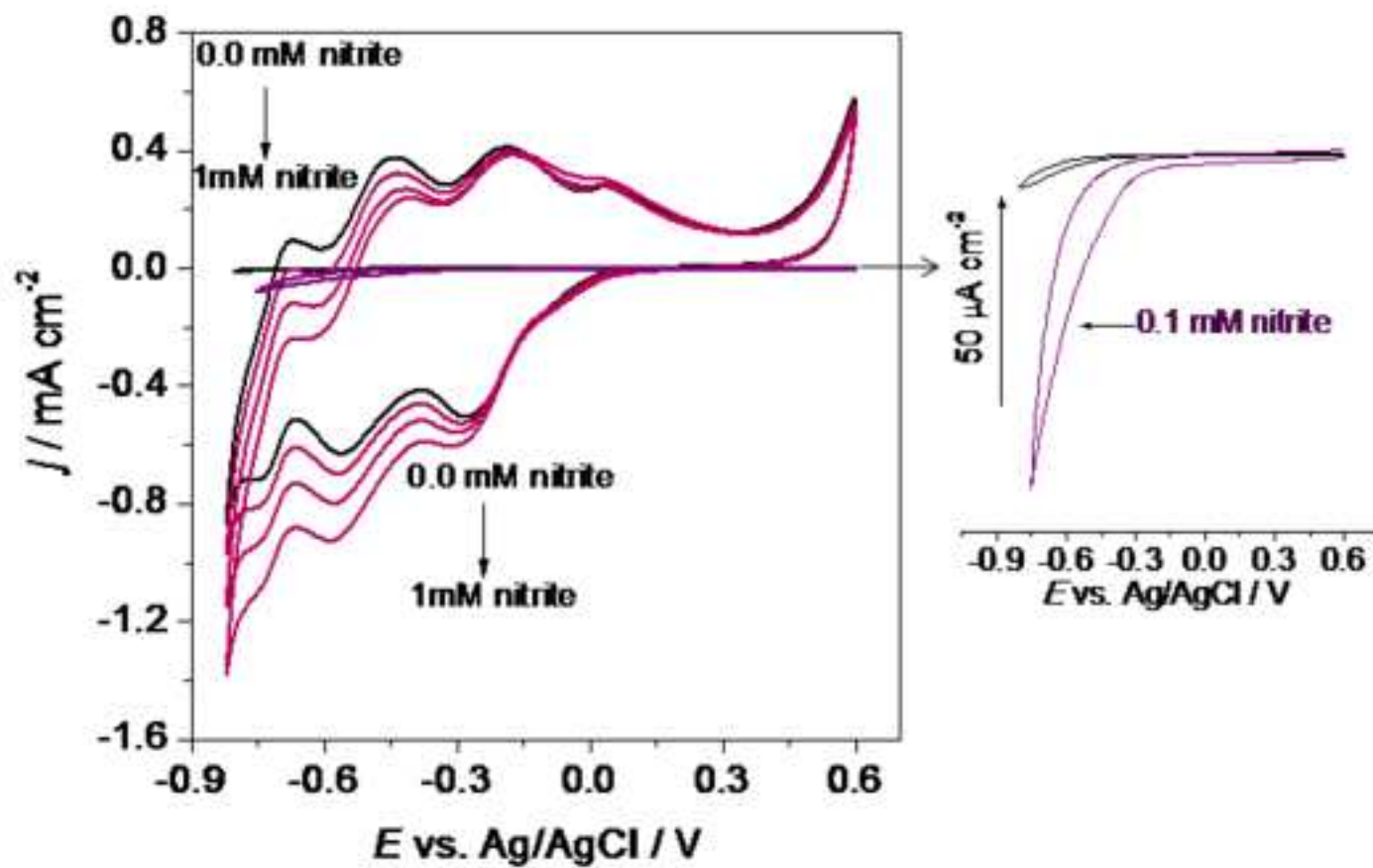


Figure 5

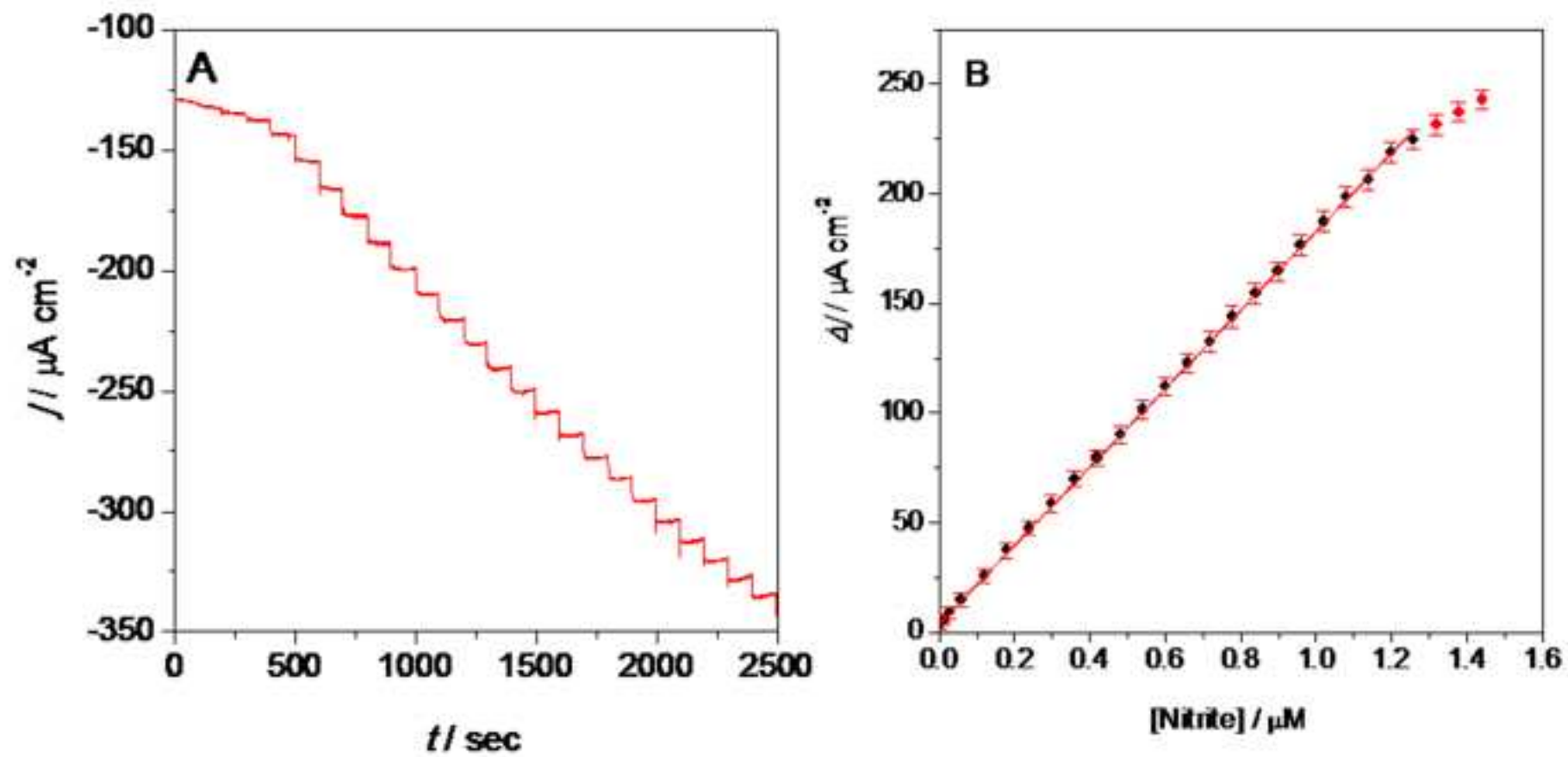


Figure 6

- Synthesized a new inorganic-organic hybrid compound consisting of SiW_{12} and Nile blue.
- Hybrid compound possess new synergy properties and poor solubility in water.
- Electroreduction of nitrite by $\text{NB}_2\text{SiW}_{12}$ modified carbon paste electrode.
- The electrode has a good mechanical and chemical stability and reproducibility.
- The proposed sensor is suitable for use in real water sample.

ACCEPTED MANUSCRIPT