

Electrochemical sensing of cyanometallic compound using TiO₂/PVA nanocomposite-modified electrode

Shrabani Mondal¹ · Rashmi Madhuri² · Prashant K. Sharma¹

Received: 25 August 2016 / Accepted: 10 November 2016 / Published online: 17 November 2016
© Springer Science+Business Media Dordrecht 2016

Abstract This paper addresses the detailed investigation on the electrochemical activity of TiO₂/PVA nanocomposite-modified pencil graphite electrode (TiO₂/PVA-PGE) in aqueous KCl medium at room temperature. Herein, we have used ferri/ferrocyanide redox couple as probe molecule and demonstrated the reversibility, surface diffusion ability, stability, and electroactive surface area of TiO₂/PVA-PGE. Formation of functional groups, structure, and the morphology of the prepared sample are examined using various characterization techniques. On top of this, the as-modified PGE is used for the first time in the voltammetric detection of potassium ferricyanide in aqueous KCl medium. The developed sensor is sensitive for only ferricyanide molecule and does not show any current response for other interfering

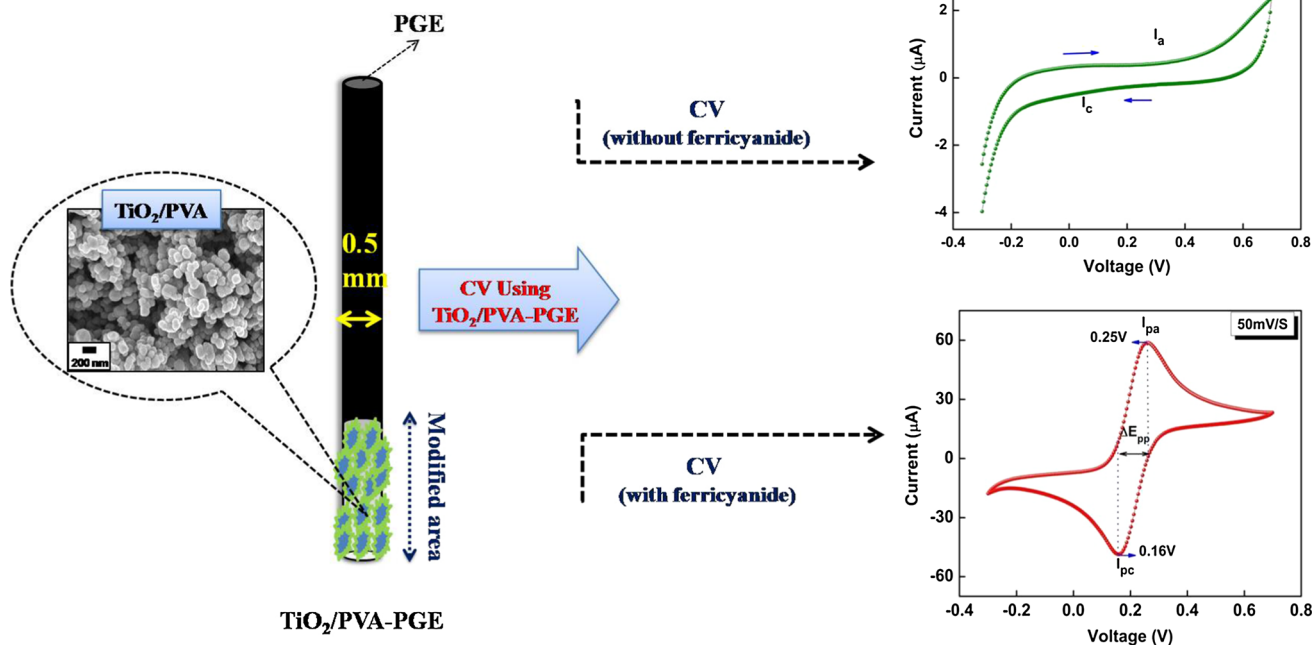
compounds such as, ascorbic acid (AA), Uric acid (UA), dopamine (DA), acetaminophen (ACOP), Hydrogen peroxide (H₂O₂), and 4-nitrophenol (4-NP) within wide linear range of 0.17–33.33 mM with a high order of correlation (0.997) having a detection limit as low as 0.15 μM. Also high sensitivity of 199.34 μA mM⁻¹ cm⁻² for oxidation current is obtained. The finding of present paper gives a very clear and concise understanding towards the role of modification on the surface electrochemistry of any bare/unmodified electrode and shows the ample possibility in the application of the prepared TiO₂/PVA nanocomposite-modified electrodes for selective electrochemical sensing of cyanometallic compound in the presence of other electroactive molecules.

✉ Prashant K. Sharma
prashantnac@gmail.com

¹ Department of Applied Physics, Functional Nanomaterials Research Laboratory, Indian Institute of Technology (Indian School of Mines), Dhanbad 826004, Jharkhand, India

² Department of Applied Chemistry, Indian Institute of Technology (Indian School of Mines), Dhanbad 826004, Jharkhand, India

Graphical Abstract



Keywords TiO₂/PVA nanocomposite · Electrochemistry · Cyclic voltammetry · Ferricyanide · Electrochemical sensor

1 Introduction

Proper understanding about the electrode's surface properties has grown tremendous interest among the research community as the working electrode always plays a crucial role in all kinds of electroanalytical and electrochemical detection. Among the carbon-based electrodes, bulk glassy carbon electrode (GCE) is one of the most frequently used macroelectrodes in electrochemical sensors [1], though its relatively high background current and cost remain the major problems. In this frame, low cost [\$0.30 per PGE, vs. \$190 + per GCE], commercially available pencil leads (pencil graphite electrode—PGE) may overcome this cost barrier. These PGE also show smaller background current, can be easily modified, possess better electrochemical reactivity, and have good mechanical rigidity [1, 2]. It is already known that sensing mechanism is a surface-dominated phenomenon and sensor parameters, viz. selectivity and sensitivity, which can be improved by increasing the roughness factor (electroactive area/geometrical area) of the electrode [3]. Modification with artificial materials is a powerful tool employed to improve the electrode functionality. In this respect, the prompt development of nanomaterials and nanotechnology has endowed us with several new

kinds of artificial materials which have brought revolution in electrode designing [4]. Nanomaterials, such as, carbon nanotubes, graphene, metal nanoparticles, metal oxides, and conducting polymers, commonly act as good modifier due to their excellent electronic, catalytic properties, and excessively larger surface area [5, 6].

Nanostructured TiO₂ and their composites are very popular due to low cost, existence in three different polymorphic phases (anatase, brookite, and rutile), and ease of synthesis. TiO₂ and their composites have multifaceted applications, ranging from energy generation/storage devices, catalyst, anode material, luminescent material, sensing element etc. [7–9]. TiO₂ is a very common choice as sensor electrode in electrochemical analysis owing to its excellent catalytic activity, long-term stability, and non-toxicity [10]. Still, application of TiO₂/PVA nanocomposite as modifier in electrochemical sensor is scantily reported in the literature. In our previous work, the detailed investigation pertaining to anatase to rutile phase transformation (ART) at very low temperature was demonstrated by introducing PVA during the reaction/synthesis [11]. We had also performed a preliminary study on the electrochemical behavior of TiO₂ and TiO₂/PVA nanocomposite and elucidated that combination of inorganic–organic hybrid material (TiO₂ and PVA) has considerably enhanced the electrochemical response. Smaller size of the nanoparticles along with larger exposure area has facilitated the electron transfer rate of the redox reaction [11]. In continuation to our previous preliminary work, in the present work, we have emphasized on the detailed

investigation of the electrochemical behavior of TiO₂/PVA nanocomposite-modified pencil graphite electrode and its sensing ability.

Potassium ferricyanide, a well-known cyanometallic compound, is treated as benchmark redox probe for evaluation of the electrochemical properties of any novel electrode [12, 13]. On the other hand, free cyanides have an important environmental issue due to their toxicity [14]. Cyanides are originated from different industrial activities such as, metal plating, mining, gas production, and pharmaceutical. Cyanides have high affinity towards gold and hence gold mine industries contribute significantly in cyanide production as an effluent after the gold extraction from its ore [15]. According to the relative toxicity level, cyanometallic compounds are less toxic than free cyanides [16]. Yet, the monitoring of them is compulsory as they are capable of generating small amount of free cyanides under the influence of sunlight via photolysis process or under other suitable environmental conditions (the absence of light but in appropriate pH value) [17]. A detailed discussion on the physiochemical processes and toxicity level of cyanides and cyanometallic compound is published by Gérald et al. in 2004 [15]. In this framework, this article gives an insight on the surface electrochemistry of TiO₂/PVA nanocomposite-modified pencil graphite electrode and its subsequent use in the voltammetric detection of potassium ferricyanide. To the best of our knowledge, TiO₂/PVA nanocomposite-modified pencil graphite electrode has not been used earlier in the detection of potassium ferricyanide.

2 Sample preparation and characterization details

2.1 Chemicals used

Titanium Chloride (TiCl₃) with 99.99% purity (Sigma Aldrich, Germany), acetaminophen (ACOP) (Sigma Aldrich, Germany), polyvinyl alcohol (PVA) (E. Merck Limited, India), MW = 145,000, Sodium hydroxide (NaOH), Hydrogen peroxide (H₂O₂), 4-nitrophenol (4-NP) and Ethanol (E. Merck Limited, India) are used as-received. Uric acid (UA) and ascorbic acid (AA) are purchased from Loba chemie, India) and dopamine hydrochloride (DA) is procured from Alfa Aesar, USA. Double-distilled water is used throughout this work. 50 mM of ferricyanide stock solution is prepared by direct dilution of potassium ferricyanide (Loba chemie, India) into KCl solution, and interferents are prepared in double-distilled water.

2.2 Synthesis procedure

The synthesis procedure is similar to the reported one in our previous work [11]. In brief, aqueous solution of TiCl₃

is prepared by adding 1 mL of it into 40 mL of NaOH (0.4 M). The colorless homogeneous solution of PVA (4 gm in 100 mL of double-distilled water, heated at 80 °C) was introduced in the NaOH solution under vigorous stirring. The as-obtained precipitate was then collected via centrifugation and washed several times with distilled water until pH became neutral. In the next step, obtained filtrate was transferred into a stainless steel autoclave, and the total volume was made 70 mL by water addition. Autoclave was kept at 180 °C for 6 h. Sample was separated out after washing several times with ethanol and water via centrifugation, and finally the powder sample was obtained after drying at 40 °C in air.

2.3 Apparatus used

The phase and structure of the sample were analyzed by X-ray diffraction (XRD, Bruker D8, USA., Cu K_α radiation). Morphology and the vibrational bonds were observed using field emission scanning electron microscope (FESEM, Supra-55, Zeiss, Germany) and fourier transformed infrared spectroscopy (FTIR, Perkin-Elmer Spectrum Bx, USA), respectively.

The electrochemical experiments were performed on a Potentiostat/Galvanostat (model: PalmSens3, PalmSens BV, The Netherlands). A conventional one compartment 3-electrode electrochemical cell equipped with counter electrode (Pt wire), reference electrode (Ag/AgCl), and working electrode (nanocomposite-modified pencil graphite electrode) was used for voltammetric measurements.

2.3.1 Preparation of TiO₂/PVA nanocomposite-modified electrode

Surface modification of bare PGE (0.5 mm diameter) with prepared nanocomposite was accomplished using dip coating method already reported in our earlier work [11]. Typically, bare PGE is first treated with 0.6 M HCl, distilled water, and rubbed with cotton. Next, prepared powder sample (1 mg) was ultrasonically dispersed into DMSO (5 mL) for half an hour. Pre-treated cleaned PGE was dipped into the solution and finally rinsed by water washing to remove any loosely bound particle. This electrode is named as TiO₂/PVA-PGE.

3 Results and discussion

3.1 Structural properties

Figure 1 shows the XRD profile of TiO₂/PVA nanocomposite. The obtained result is similar to the previously reported work of our group [11]. Intense reflection peak observed at

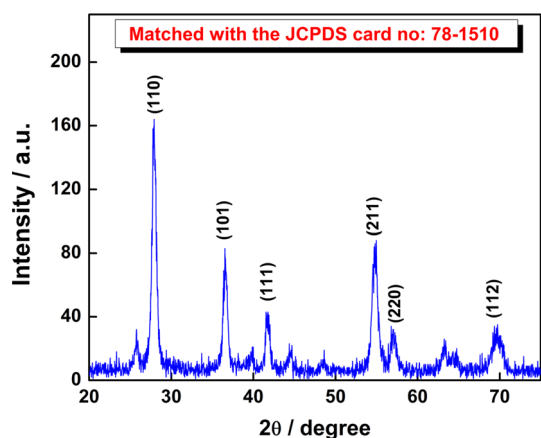


Fig. 1 XRD pattern of TiO₂/PVA nanocomposite

$2\theta = 27.9^\circ$ indicates the rutile structure of prepared nanocomposite. All of the diffraction peaks are well matched with the JCPDS Card No. 781510. Crystallite size calculated using Debye–Scherrer formula for the major prominent peaks is 8–11 nm. A detailed discussion is available in Ref. [11]. Figure 2a elucidates the FTIR spectrum of TiO₂/PVA nanocomposite. As seen from the spectrum, the peak at 520 cm^{-1} corresponds to the Ti–O–Ti asymmetric stretching [18], 1636 cm^{-1} for the TiO₂ and absorbed water interaction, and 2921 cm^{-1} band originates for C–H vibration of PVA [19]. Morphology of the prepared sample is observed using FESEM image presented in Fig. 2b. Wide distribution of spherical-shaped particles is seen.

3.2 Electrochemical characteristics of TiO₂/PVA-PGE

In our previous study [11], we have presented a very preliminary comparative study on the electrochemical

responses of pure TiO₂ and TiO₂/PVA-modified PGE. Finding of the work showed that the TiO₂/PVA-modified PGE possessed better electron transfer ability than pure TiO₂-modified electrode. The current response on TiO₂/PVA-PGE is 1.5-fold larger than TiO₂-PGE. This improved response was attributed to the formation of smaller sized nanoparticles after incorporating PVA which provided larger surface area compared to the pure TiO₂ nanoparticles. Also, highly reactive hydroxyl [–OH] ions of polymer chains served as conducting path along electrolyte–electrode interface resulting better transportation of charge carriers. Herein, we have illustrated our previous work and investigated in detail the electrode parameters of the TiO₂/PVA-PGE using Fe(CN)₆^{3–/4–} redox reaction as model system. Thereafter, real analytical application was demonstrated for the detection of the cyanometallic compound K₃Fe(CN)₆.

The electrochemical behavior of TiO₂/PVA-PGE was firstly investigated by cyclic voltammetry using aqueous KCl as supporting electrolyte within the potential window of -0.3 V to $+0.7\text{ V}$ vs Ag/AgCl electrode. Amongst all electrochemical methods, cyclic voltammetry is the most convenient, versatile and routinely applied technique for determining the electrode properties [20]. CV contains a wide range of information regarding the electrochemical process viz. accurate location of oxidation/reduction potentials, electrode kinetics, number of electron involved, electroactive area of the electrode, diffusion coefficient and also the concentration of analyte molecule. In a reversible reaction, linearly scanning potential in the form of a triangular wave is applied back and forth (forward/reverse) direction in the presence of electroactive species to generate rapid redox products. Potassium ferricyanide is used as electroactive substance in this case. Typical voltammogram obtained on TiO₂/PVA-PGE at scan rate 50 mV s^{-1} is shown in Fig. 3. Well-defined

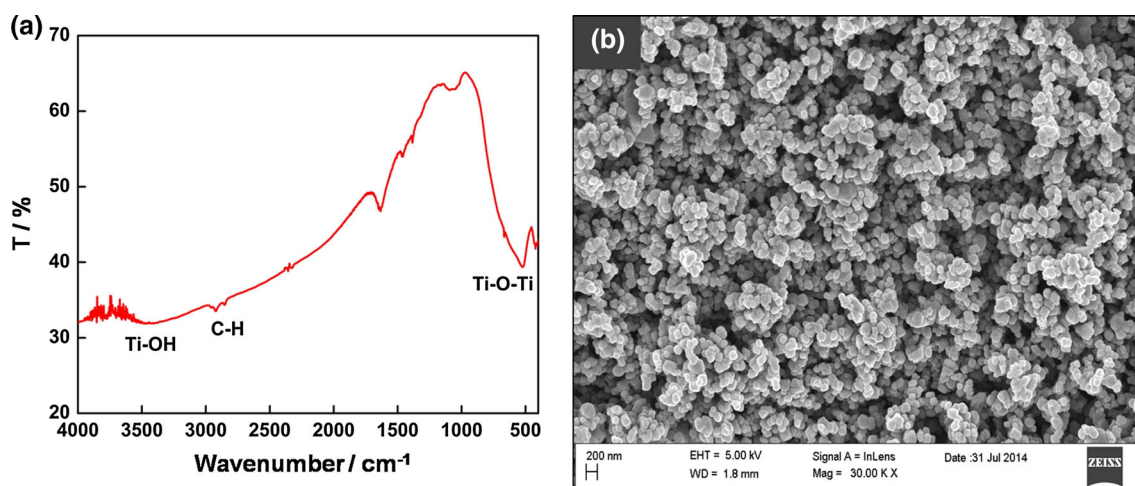


Fig. 2 a FTIR spectrum and b FESEM image of TiO₂/PVA nanocomposite

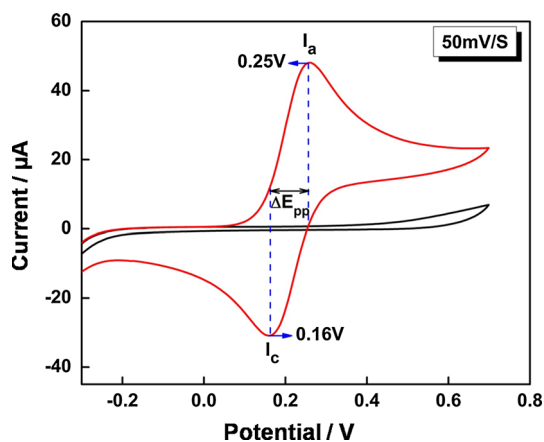
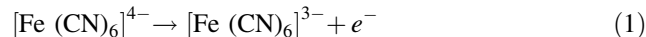


Fig. 3 CV profile of TiO₂/PVA-modified pencil graphite electrode in the presence/absence of ferricyanide in KCl electrolyte

redox peaks within the scanned potential range are observed only after the introduction of K₃Fe(CN)₆. On the other hand, no peaks are observed for the blank run (without probe molecule). Hence, these peaks at 0.25 and 0.16 V can be easily ascribed to the conversion of ferri to ferro and vice versa according to the following electron transfer reaction:



Minute observation reveals that the peak-to-peak separation of the ferri/ferro couple (ΔE_{pp}) is 90 mV. This small value of ΔE_{pp} gives direct indication of the better electron transfer kinetic and low resistance in TiO₂/PVA-PGE. We also observed that the ratio of peak current (I_a/I_c) is $\cong 1.2$,

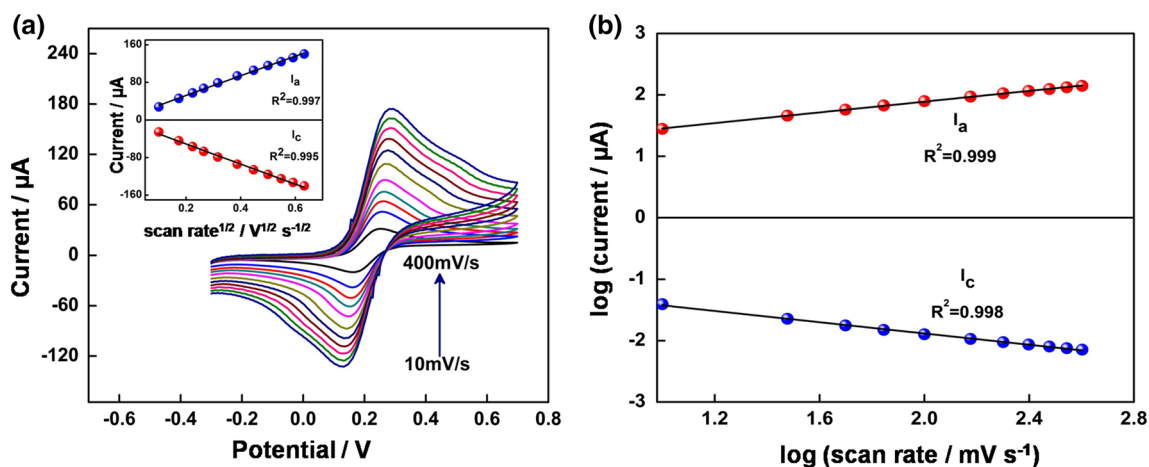


Fig. 4 **a** CV of TiO₂/PVA-modified electrode at different scan rates and **b** the plot of $\log(\text{current}/\mu\text{A})$ against $\log(\text{scan rate}/\text{mV s}^{-1})$. Inset of **a** shows linear fitted plot of peak current vs scan rate

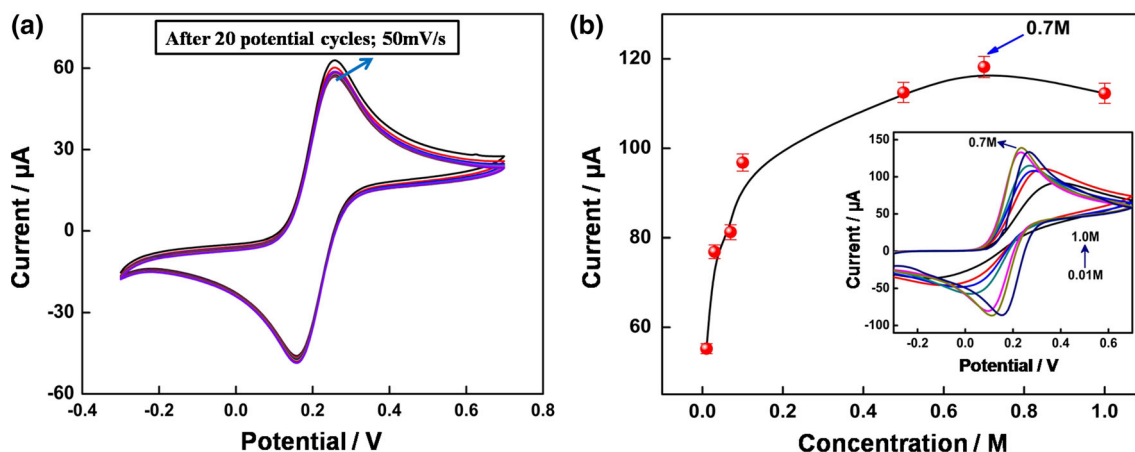


Fig. 5 **a** The repeatability of the TiO₂/PVA-modified electrode after 20 CV cycle at 50 mV S⁻¹. **b** The cyclic voltammograms obtained at different KCl concentrations on TiO₂/PVA-modified electrode

Table 1 Important electrode parameters characterizing the ferri/ferro redox probe at scan rate 50 mV/s

Electrode	E_{pa} (V)	E_{pc} (V)	ΔE_{pp} (V)	ΔE_{pa} (V)	I_d/I_c	Electroactive area (cm^2)
TiO ₂ /PVA-PGE	0.25	0.16	0.09	0.03	1.2	3.8×10^{-5}

which slightly differs from the exact value of 1.0. This indicates the quasi-reversibility of the redox reaction on TiO₂/PVA-PGE.

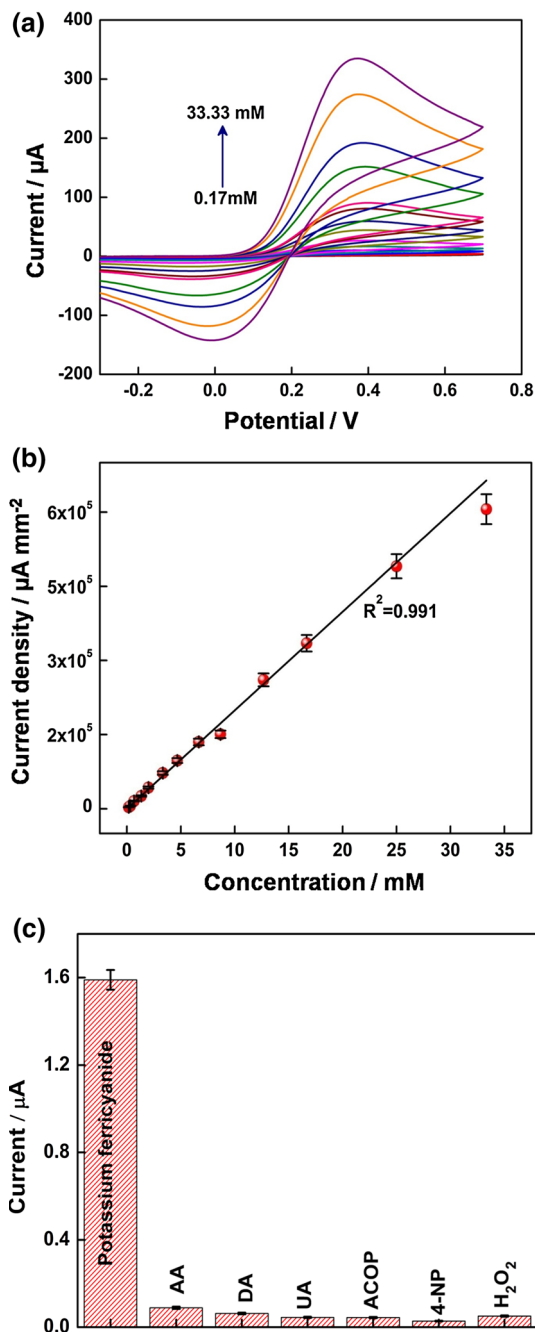


Fig. 6 a Cyclic voltammetry of ferricyanide at concentration range of 0.17 to 33.33 mM L⁻¹ in 0.7 M KCl on TiO₂/PVA-modified electrode. b The calibration plot of peak current density and concentration. c Interference studies in presence of some electroactive molecules

In order to investigate the scan rate dependence on the redox reaction, two distinct set of CV measurements were performed, by varying the scan rate and by increasing the number of cycles at fixed scan rate. Both the anodic and cathodic peak currents increase (Fig. 4a) with square root of scan rates in the entire tested region of 10–400 mV s⁻¹. This linear dependence of the aforementioned parameters at the TiO₂/PVA-PGE surface might be due to the adsorption of ferricyanide at the active sites of nanocomposite-modified working electrode. Kinetic analysis of the TiO₂/PVA-PGE is performed by plotting the logarithm of current against logarithm of scan rate. The linear regression equations obtained for log I_a and log I_c are $Y = 0.436 X + 1.016$; ($R^2 = 0.999$), $Y = 0.459 X + 0.964$; ($R^2 = 0.998$), respectively. The experimental slopes of ~ 0.44 and 0.46 (Fig. 4b) slightly differ from the theoretical value of 0.5. This suggests that the electrochemical process is diffusion-controlled process. This discrepancy from theoretical value arises due to the solution resistance. Moreover, the shift in peak potential (ΔE_{pa}) with scan rate is 0.03 V, almost negligible to the change in scan rate. After 20 cycles of CV run at potential sweep rate 50 mV s⁻¹ (Fig. 5a) peak currents remain almost constant (only 8% decrease in peak current after 20 cycle), implies that the modification of nanocomposite onto the PGE is electrochemically stable and suitable for electrochemical sensing. This excellent stability of the modified electrode over repetitive scans can be attributed to the superior adhesive nature of PVA.

As already known, electroactive surface area of any modified electrode is one of the most interesting as well as important parameters than its geometrical area. Geometrical area is the simple sum of all the physical areas covering the electrode surface. On contrary, electroactive/real surface area of the electrode represent the area which took part in the electron exchange process [21]. The kinetic parameters of the reaction are dependent on this factor. Cyclic voltammetry is the easiest method/tool to calculate the electroactive area of the PGE. In general, any diffusion-controlled reversible/quasi-reversible electrochemical process follows the famous Randles–Sevcik equation [22, 23]:

$$i_p = 2.69 \times 10^5 D_0^{1/2} n^{3/2} v^{1/2} C_0 A, \quad (3)$$

where i_p is the peak current; n represents the number of electron transferred; D_0 is the diffusion coefficient of the electroactive species ($\text{cm}^2 \text{s}^{-1}$); C_0 is the bulk concentration (0.01 mol L^{-1}) of the same species; V is the scan rate

(V s⁻¹), and *A* represents the electroactive area (cm²) of the electrode. Using the voltammogram data of ferri/ferro redox reaction (one electron transfer process), the calculated electroactive surface area after modification is 3.8 × 10⁻⁵ cm² having the roughness factor of 5.9 × 10⁻⁴. This higher value of effective surface area provided by nanocomposite is suitable for sensing applications. Evaluated electrochemical parameters for TiO₂/PVA-PGE are listed in Table 1.

4 Analytical application

4.1 Sensing of cyanometalic compound

In addition of determining the electrode properties, we have also examined the suitability of the developed electrode in sensing application. For the purpose, a real analytical application was demonstrated for the detection of the cyanometalic compound, K₃Fe(CN)₆. Figure 5b elucidates the CV result for 1 mM ferricyanide in different ionic strengths of supporting electrolyte (KCl) at potential sweep

rate of 50 mV s⁻¹. Different magnitudes of peak currents and their ratio corresponding to each electrolyte concentration confirm the active role of electrolyte in redox reaction. 0.7 M is found to be the optimum concentration when TiO₂/PVA-PGE exhibits maximum peak current as well as redox reversibility (1.02 ≅ theoretical value 1.0). To evaluate the sensor parameters, sensitivity and detection limit, the concentration of target (potassium ferricyanide) is varied by successive addition of desired amount of stock solution at a regular step of concentration. As shown in Fig. 6a, oxidative current obtained from the voltammogram linearly increases with the concentration for the above-mentioned range (0.17–33.33 mM) with a high order of correlation coefficient (*R*² = 0.991). Calibration plot (Fig. 6b) bears a linear relationship: *J* (A cm⁻²) = 199.34*C* (mM) – 248.75. A detection limit of 0.15 μM with a high sensitivity of 199.34 μA mM⁻¹ cm⁻² was obtained using calibration plot. A comprehensive comparison of our results with previously reported work is provided in Table 2. As seen from the table, the developed ferricyanide sensor showed better performance in terms of sensitivity as well as detection limit.

Table 2 Comparison of several previously reported potassium ferricyanide sensors

Electrode	Detection limit (μM)	Sensitivity μA mM ⁻¹	Linear range	Reference
APS-MCPE ^a	0.08	–	0.2–10 μM	[14]
MWCNT/TiO ₂ /GCE ^b	48.6, 1.1	77.6, 68.9	0.01–0.2 mM	[24]
VA MWCNTs ^c	28.23	71.5 cm ⁻²	–	[25]
HRO MWCNTs ^d	78.56	62.8 cm ⁻²	–	[25]
SDS/CPE ^e	100	–	–	[26]
TiO ₂ /PVA-PGE	0.15	199.34 cm ⁻²	0.17–33.33 mM	Present work

^a APS-MCPE aminopropyl-grafted mesoporous silica-modified carbon paste electrode

^b MWCNT/TiO₂/GCE multi-wall carbon nanotubes/titanium dioxide composite-modified glassy carbon electrode

^c VA MWCNTs vertically aligned multi-wall carbon nanotubes

^d HRO MWCNTs horizontally/randomly oriented multi-wall carbon nanotubes

^e SDS/CPE sodium dodecyl sulfate-modified carbon paste electrode

Table 3 Interference test results of potassium ferricyanide sensor in the presence of electroactive molecules

Analyte	Concentration of analyte (mM)	Obtained current (μA)	Current response with respect to potassium ferricyanide (%)
Potassium ferricyanide	0.2	1.590	100
AA	0.2	0.089	5.5
DA	0.2	0.063	3.9
UA	0.2	0.045	2.8
ACOP	0.2	0.044	2.7
4-NP	0.2	0.028	1.7
H ₂ O ₂	0.2	0.051	3.2

4.2 Interference studies

To ensure the selectivity of the prepared potassium ferricyanide sensor, CV responses were recorded at the optimized conditions in presence of other electroactive molecules viz. AA, UA, DA, ACOP, 4-NP, and H₂O₂. As seen in the histogram (Fig. 6c), the interfering species have generated nearly negligible current response as compared to the same concentration of ferricyanide (0.2 mM). Obtained results are depicted in Table 3. The interference studies confirm that the developed sensor has specific response to potassium ferricyanide and can be used for selective electrochemical sensing of cyanometallic compounds in the presence of other electroactive molecules.

5 Conclusions

The detailed investigation on the electrochemical properties of TiO₂/PVA-modified pencil graphite electrode with respect to the probe molecule ferri/ferrocyanide redox couple has been performed. Electroactive surface area and redox reversibility along with the electrochemical stability of the modified electrode are determined. The TiO₂/PVA-modified pencil graphite electrode is successfully applied in the voltammetric detection of cyanometallic compound potassium ferricyanide. The fabricated TiO₂/PVA nanocomposite sensor is sensitive for only ferricyanide molecule and does not show any current response for other interfering compounds such as, ascorbic acid (AA), Uric acid (UA), dopamine (DA), acetaminophen (ACOP), Hydrogen peroxide (H₂O₂), and 4-nitrophenol (4-NP) with a wide linear concentration region of 0.17 mM to 33.33 mM having a high sensitivity of 199.34 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ and detection limit as low as 0.15 μM . Our work shows the ample possibility in the application of the prepared TiO₂/PVA nanocomposite-modified electrodes for selective electrochemical sensing of cyanometallic compounds in the presence of other electroactive molecules.

Acknowledgements The authors are thankful to Department of Science and Technology, Government of India for sanction of Fast Track Research Project for Young Scientists to Dr. Prashant K. Sharma (Ref. No.: SR/FTP/PS-157/2011) and Dr. Rashmi Madhuri (Ref. No.: SB/FT/CS-155/2012). Dr. Sharma (FRS/34/2012-2013/APH) and Dr. Madhuri (FRS/43/2013-2014/AC) are also thankful to Indian School of Mines, Dhanbad for grant of Major Research Project under Faculty Research Scheme. The authors are also thankful to Board of Research in Nuclear Sciences (BRNS), Department of Atomic Energy, Government of India for major research project (Sanction No. 34/14/21/2014-BRNS/0295). The authors also sincerely acknowledge the facilities available in Central Research Facility of the Institute. Shrabani is also thankful to Indian School of Mines, Dhanbad for Senior Research Fellowship.

References

- Özcan A, Şahin Y (2011) A novel approach for the determination of paracetamol based on the reaction of *N*-acetyl-*P*-benzoquinoneimine formed on the electrochemically treated pencil graphite electrode. *Anal Chim Acta* 685:9–14
- Gowda JI, Nandibewoor ST (2012) Electrochemical behavior of 4-aminophenazone drug at a graphite pencil electrode and its application in real samples. *Ind Eng Chem Res* 51:1594–15936
- Patel F (1992) The fatal paracetamol dosage—how low can you go? *Med Sci Law* 32:303–310
- Afkhami A, Khoshsafar H, Bagheri H, Madrakian T (2014) Preparation of NiFe₂O₄/graphene nanocomposite and its application as a modifier for the fabrication of an electrochemical sensor for the simultaneous determination of tramadol and acetaminophen. *Anal Chim Acta* 831:50–59
- Shrama PK, Rudowicz C, Pandey AC, Zolnierkiewicz G, Guskos N (2009) Relationship between oxygen defects and the photoluminescence property of ZnO nanoparticles: a spectroscopic view. *J Appl Phys* 106:094314–094319
- Dutta RK, Shrama PK, Pandey AC (2010) DNA base, cytosine modified/capped ultrasmall Gd₂S₃: Eu³⁺ gadofluoroprobes for platelet isolation. *Appl Phys Lett* 97:253702–253705
- Zhu S, Liang S, Gu Q, Xie L, Wang J, Ding Z, Liu P (2012) Effect of Au supported TiO₂ with dominant exposed 0 0 1 facets on the visible-light photocatalytic activity. *Appl Catal B* 146:119–120
- Du J, Qi J, Wang D, Tang Z (2012) Facile synthesis of Au@TiO₂ core-shell hollow spheres for dye-sensitized solar cells with remarkably improved efficiency. *Energy Environ Sci* 5:6914–6918
- Silva CG, Juarez R, Marino T, Molinari R, Garcia H (2011) Influence of excitation wavelength (UV or visible light) on the photocatalytic activity of titania containing gold nanoparticles for the generation of hydrogen or oxygen from water. *J Am Chem Soc* 133:595–602
- Fujishima A, Rao TN, Tryk DA (2000) Titanium dioxide photocatalysis. *J Photochem Photobiol, C* 1:1–21
- Mondal S, Madhuri R, Sharma PK (2015) PVA assisted low temperature anatase to rutile phase transformation (ART) and properties of titania nanoparticles. *J Alloys Compd* 646:565–572
- Chen P, McCreery RL (1996) Control of electron transfer kinetics at glassy carbon electrodes by specific surface modification. *Anal Chem* 68:3958–3965
- Pandey PC, Upadhyay BC (2005) Studies on differential sensing of dopamine at the surface of chemically sensitized ormosil-modified electrodes. *Talanta* 67:997–1006
- Ojani R, Ahmadi E, Raoof JB, Mohamadnia F (2009) Characterization of a carbon paste electrode containing organically modified nanostructure silica: application to voltammetric detection of ferricyanide. *J Electroanal Chem* 626:23–29
- Zagury GJ, Oudjehani K, Deschênes L (2004) Characterization and availability of cyanide in solid mine tailings from gold extraction plants. *Sci Total Environ* 320:211–224
- Shifrin NS, Beck BD, Gauthier TD, Chapnick SD, Goodman G (1996) Chemistry, toxicology, and human health risk of cyanide compounds in soils at former manufactured gas plant sites. *Chemistry* 23:106–116
- Meeussen JCL, Keizer MK, Haan FAMD (1992) Chemical stability and decomposition rate of iron cyanide complexes in soil solutions. *Environ Sci Technol* 26:511–516
- Kavitha B, Dasharatham D, Srinivasu D, Srinivas CH, Narsimlu N (2011) Synthesis and characterization of TiO₂ doped polyvinyl alcohol polymer composites. *J Chem Pharm* 4:155–157

19. Liu L, Zhao C, Yang F (2012) TiO₂ and polyvinyl alcohol (PVA) coated polyester filter in bioreactor for wastewater treatment. *Water Res* 46:1969–1978
20. Kissinger PT, Heineman WR (1983) Cyclic Voltammetry. *J Chem Educ* 60:702–706
21. Adolphe X, Martemianov S, Palchetti I, Mascini M (2005) On the electrochemical flow measurements using carbon-based screen-printed electrodiffusion probes. *J Appl Electrochem* 35:599–607
22. Gooding JJ, Praig VG, Hall EA (1998) Platinum-catalyzed enzyme electrodes immobilized on gold using self-assembled layers. *Anal Chem* 70:2396–2402
23. Brett CMA, Brett AMO (1993) *Electrochemistry: principles, methods, and applications*. Oxford Science Publications, Oxford, pp 103–109
24. Perenlei G, Tee TW, Yusof NA, Kheng GJ (2011) Voltammetric detection of potassium ferricyanide mediated by multi-walled carbon nanotube/titanium dioxide composite modified glassy carbon electrode. *Int J Electrochem Sci* 6:520–531
25. Taurino I, Carrara S, Giorcelli M, Tagliaferro A, Micheli GD (2012) Comparison of two different carbon nanotube-based surfaces with respect to potassium ferricyanide electrochemistry. *Surf Sci* 606:156–160
26. Niranjana E, Swamy BEK, Naik RR, Sherigara BS, Jayadevappa H (2009) Electrochemical investigations of potassium ferricyanide and dopamine by sodium dodecyl sulphate modified carbon paste electrode: a cyclic voltammetric study. *J Electroanal Chem* 631:1–9