



Graphene–Polyaniline composite based ultra-sensitive electrochemical sensor for non-enzymatic detection of urea



Rinky Sha^a, Kikuo Komori^{b,c}, Sushmee Badhulika^{a,*}

^a Department of Electrical Engineering, Indian Institute of Technology, Hyderabad 502285, India

^b Department of Chemical System Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

^c Institute of Industrial Science, University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8505, Japan

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ABSTRACT

Detection of urea is of prime importance in food and water safety, dairy industries and environmental monitoring. Traditional methods to detect urea are either expensive and involve sophisticated instrumentation or are based on enzymatic approach of detection. Herein, we report a Graphene-Polyaniline (Gr-PANI) based electrochemical sensor for non-enzymatic detection of urea. Gr-PANI composite was synthesized by electro-deposition of PANi on the surface of Gr modified GCE using cyclic voltammetry (CV) technique. The presence of Gr and PANi in the composite was confirmed using a multitude of characterization techniques which included FESEM, XRD and Raman spectroscopy. The electrochemical behavior of urea at the surface of Gr-PANI modified GCE was studied by CV whereas urea sensing was performed by using simple current-potential (I–V) technique. The current response of the as-fabricated urea sensor was ~ 4.74 folds greater than that of pure PANi based sensor and ~ 67.2 times greater than that of pure Gr based sensor. The sensing performance of the composite based urea sensor was optimized by varying the thickness of PANi film. The optimized sensor exhibited lower limit of detection ($5.88 \mu\text{M}$), excellent reproducibility, selectivity and stability with an enhanced sensitivity of $-226.9 \mu\text{A}/\mu\text{M cm}^2$ ($R^2 = 0.993$) in the range of $10 \mu\text{M}$ – $200 \mu\text{M}$. The reliability of the as-fabricated sensor was successfully investigated by using it to detect urea concentrations in samples of tap water and milk samples. This highly-sensitive Gr-PANI composite based urea sensor provides a simple, low cost, non-enzymatic approach for detection of urea that find numerous applications in clinical diagnostics, dairy industries, fertilizer plants and environmental monitoring.

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1. Introduction

Urea is a common organic compound and one of the primary products in protein metabolism. Higher levels of urea in blood and urine causes kidney failure, urinary tract obstruction, gastrointestinal bleeding, dehydration, burns and shock, while lower level of urea results in hepatic failure, nephritic syndrome and cachexia [1,2]. Urea is one of the most common adulterants in milk, higher concentrations of which causes indigestion, ulcers, acidity etc. [3]. Urea is also introduced into the environment as fertilizer, where it decomposes to toxic ammonia, thereby polluting the environment [4]. Thus, the accurate detection of urea is of prime importance in clinical diagnostics, dairy industries, fertilizer plants and environmental monitoring.

Most common methods used for urea detection include solid phase extraction, ultraviolet-visible spectroscopy, infra-red (IR) spectroscopy, flow injection, ion chromatography, liquid chromatography-mass spectrometry, fluorimetry and surface plasmon resonance etc. [3,5,6]. These conventional methods are often high cost, require sophisticated instrumentation, time consuming complex sample pre-treatments which make them unsuitable for on-site monitoring. To address these issues, electrochemical sensors have gained significant attention for direct detection and quantitative estimation of urea owing to their higher sensitivity, simplicity, faster response, low cost [3]. Electrochemical detection of urea is performed on both enzymatic [7] and non-enzymatic platforms [8,9]. Enzymatic urea sensors use urease as an enzyme for its detection. The major drawbacks of enzymatic urea sensors are immobilization of enzymes, high cost, lack of reproducibility, and limited working conditions such as temperature, pH and humidity [3]. In non-enzymatic approach, urea is detected through its oxidation/reduction on suitable electrodes [1,9]. For

* Corresponding author. Tel.: +040 23018443.
E-mail address: sbadh@iith.ac.in (S. Badhulika).

electrochemical sensing of urea, amperometry [9], electrochemical impedance spectroscopy (EIS) [1], differential pulse voltammetry (DPV) [10], potentiometry [7], cyclic voltammetry [11], current-potential (I–V) techniques [12,13] have been reported in literature. In this work, a simple and reliable I–V technique was employed for electrochemical urea sensing.

PANi is a well-known and widely used conducting polymer in the field of electrochemical sensing due to its properties like high conductivity, low cost, high chemical durability, environmental stability and ease of synthesis [14]. PANi based potentiometric biosensor has been explored for urea sensing [4]. Similarly, Gr exhibits excellent physical and electrochemical properties such as excellent electron mobility, higher thermal conductivity, larger specific surface area, wider electrochemical potential window that enables its widespread use in electrochemical sensing [15]. Srivastava et al. [11] synthesized multilayer Gr for enzymatic urea sensing while Kumar et al. [5] demonstrated Gr nanoplatelets based enzymatic urea sensor. In order to achieve enhanced sensitivity and lower limit of detection, the composites of organic (e.g. PANi) and inorganic (e.g. Gr) semiconductor have gained much attention in electrochemical sensors [16]. In this study, we demonstrate an enzyme free, novel Gr-PANi composite based electrochemical sensor for the detection of urea. Various methods such as in situ chemical synthesis, electro-deposition, chemical mixing of Gr and PANi powder, templated growth of PANi on Gr etc., have been reported in literature to synthesize Gr-PANi composites [17–20]. Here, electro-deposition technique has been performed to deposit PANi on the surface of Gr modified GCE to synthesize Gr-PANi composite. This method has been chosen mainly because it offers a simple, low cost and controlled approach of synthesizing nano-composite film with unique morphology and distribution by tuning the deposition parameters using the versatility of electro-deposition technique. Further, it eliminates the complexities associated with other techniques such as high precursor loading, high temperature synthesis, template removal, multi-step processing step etc. Moreover, the higher surface area of Gr provides additional polymerization sites for the nucleation and growth of PANi. Non enzymatic urea sensing was carried out in 0.1 M phosphate buffer solution (PBS) of pH 7. With the successive addition of urea, the current response of the composite modified GCE decreased. The composite based sensor exhibited enhanced sensitivity towards urea than that of pristine Gr and pristine PANi modified sensors, combining the synergistic effects of both Gr and PANi. The as-fabricated urea sensor exhibited higher sensitivity, stability, selectivity, reproducibility and lower limit of detection compared to other reported literature. Furthermore, the reliability of the sensor was successfully investigated in real samples like tap water and milk spiked with known concentrations of urea. Thus, this composite modified GCE sensor offers a simple, non-enzymatic, and low cost detection of urea in clinical diagnostics, dairy industries, fertilizer plants and environmental monitoring. To the best of our knowledge, no other studies have been reported on Gr-PANi composite based non-enzymatic urea sensor using a simple I–V technique.

2. Experimental

2.1. Materials

Gr flakes (average flake thickness: 12 nm (30–50 monolayers)) were procured commercially from Graphene supermarket, US. Aniline, sulfuric acid (H_2SO_4), N, N-dimethylformamide (DMF) [$(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$], acetone, urea (NH_2CONH_2), potassium dihydrogen phosphate (KH_2PO_4), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), uric acid, glucose, ascorbic acid were procured from Sigma Aldrich and used in the experiments as received. DI water from a

Millipore system ($\sim 18.2 \text{ M}\Omega \text{ cm}$) was used throughout the experiments.

2.2. Apparatus

Electrochemical measurements were performed on CHI 660E electrochemical workstation at room temperature at the scan rate of 50 mV/sec. A three electrode cell configuration in which Gr-PANi composite modified GCE (3 mm in diameter) as the working electrode, Ag|AgCl electrode as the reference electrode and Pt wire as the counter electrode was employed whilst 0.1 M phosphate buffer solution (PBS, pH 7.0) was used as the electrolyte for urea sensing.

2.3. Electrochemical sensor design and fabrication

Prior to the electrode modification, GCE was polished with alumina powders (0.3 and 0.05 μm), and ultra-sonicated in DI water for 5 min. 0.5 wt.% Gr was dissolved in DMF and this solution was continuously stirred at 1000 rpm for 2 h in order to obtain Gr stock solution. A 5 μL of the stock solution was drop-casted onto the cleaned GCE surface and dried at 60 $^\circ\text{C}$ in an oven for 10 min. Then, this Gr modified GCE was subjected to electro-polymerization using CV. In order to obtain Gr-PANi modified GCE, the electro-polymerization was carried out on the surface of Gr coated GCE in a potential range of -0.4 V to $+1.1 \text{ V}$ (vs. Ag|AgCl) in 0.5 M H_2SO_4 electrolytic solution containing 0.1 M aniline at the scan rate of 50 mV/sec. After electro-deposition, the Gr-PANi composite modified electrode was washed with DI water and then dried which would be used as urea sensor. To compare the sensing performances, GCE was also modified with pristine Gr or PANi.

2.4. Characterization of materials

Morphology of the as-synthesized materials were characterized by field emission scanning electron microscope (FE-SEM) operated at an accelerating voltage of 5 kV. The phase information and crystallinity of the as-prepared samples were determined by Raman spectroscopy and X-ray diffraction (XRD) respectively. XRD experiments were carried out using $\text{Cu K}\alpha$ (wavelength 1.54 \AA) line on X'pert PRO X-ray diffractometer. XRD patterns were recorded in the 2θ range 5–40 $^\circ$, θ being Bragg's diffraction angle. Raman spectra were collected in the spectral range 700–3500 cm^{-1} using 532 nm excitation source on Senterra, Bruker spectrometer.

3. Results and discussions

3.1. Synthesis of Gr-PANi composite film

Electro-deposition provides an efficient and versatile route for the synthesis of nanostructured polymers and their composites [20]. Here, the Gr-PANi composite film was synthesized by the electro-polymerization of aniline (0.1 M) in 0.5 M H_2SO_4 solution on the surface of the Gr modified GCE. Fig. 1 presents the cyclic voltammograms recorded during the electro-deposition of PANi onto Gr coated GCE. CV was carried out in the potential range of -0.4 V to $+1.1 \text{ V}$ with a scan rate of 50 mV/sec for 20 cycles. Peak current increases with increasing number of scans which indicates the formation of PANi film on the surface of Gr modified GCE. PANi has three oxidation states; (a) the fully reduced leucoemeraldine (LEB), (b) the partially oxidized emeraldine (EM), and (c) the fully oxidized pernigraniline (PNG) state. The first set of a redox peaks 1–1' corresponds to the conversion of LEB to EM and the second set of redox couple 2–2' corresponds to the conversion EM to PNG form

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