

Conducting polyaniline/reduced graphene oxide-modified carbon paste electrode for the electrochemical multi-detection of ascorbic acid and uric acid

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Abstract:

This study presents a simultaneous electrochemical detection of ascorbic acid (AA) and uric acid (UA) using fabricated polyaniline/reduced graphene oxide-modified carbon paste electrode (PANI/rGO-mCPE). PANI/rGO was synthesized via *in situ* chemical polymerization route, and characterized using FTIR, SEM, and 4-point conductivity probe. The sensor's performance was evaluated towards standard solutions of AA and UA. FTIR and conductivity studies proved that PANI/rGO composite was successfully synthesized. The FTIR spectrum of PANI/rGO shows the characteristic peaks of PANI: 3300-3500 cm⁻¹ (amine N-H bonds); 1400-1750 (aromatic rings). Combining PANI and rGO provided enhanced conductivity and surface area as compared to pristine PANI and rGO. Voltammetric studies showed direct proportional relationship between anodic peak current against analyte concentration. Based on voltammetric studies, the redox capability of synthesized electrodes was found to show an increasing trend of CPE < PANI-mCPE < PANI/rGO-mCPE. Among the three tested electrodes, the fabricated PANI/rGO-mCPE exhibited the best performance for the multi-detection of AA and UA.

Key words: polyaniline, reduced graphene oxide, multi-detection, voltammetry

1. Introduction

Ascorbic acid and uric acid play important roles in metabolism systems [1]; thus, concentrations of these acids may serve as biomarkers of physiological conditions. AA level, for instance, is related to oxidative stress [2], while extreme abnormal concentrations of UA signal possible gout or hyperuricemia [3]. High-performance liquid chromatography (HPLC), which employs different detectors, is commonly used in simultaneous AA and UA determination. However, the instrument involved is expensive, and requires trained personnel to operate. Also, this technique suffers from low sensitivity and selectivity [3-5]. With these aforementioned considerations, there is still a high interest in developing low-cost devices that operate in facile and fast way, and that can measure 2 or more target analytes in a single sensor exposure. This particular study was, hence, geared towards the construction of polyaniline/reduced graphene oxide-modified

carbon paste electrode for the multi-detection of ascorbic acid and uric acid.

2. Methodology

Reduced graphene oxide was prepared using Hummer's method [6]. H₂SO₄ (98%, 120mL), graphite (3.0g), and NaNO₃ (1.5g) were mixed, and the resulting mixture was stirred for 2h in an ice bath. After stirring, KMnO₄ (18g) was added slowly. The solution was stirred for 18h in a H₂O bath, which resulted to a dark green solution. Cold distilled H₂O (850mL) was added and stirred for 30min. Excess KMnO₄ was eliminated from the solution by adding 3mL of H₂O₂ dropwise under stirring for 2h. The solution was filtered, and washed with HCl, deionized H₂O, and ethanol. It was centrifuged and the supernatant was subjected to osmosis, then the GO solution was freeze-dried. **PANI/rGO** was prepared via *in situ* chemical oxidative polymerization. Aniline:GO (1:5), and 1 M HCl were added to double distilled H₂O. This mixture was stirred for 30min at RT.

(NH₄)₂S₂O₈ was added to the resulting mixture with continuous stirring for 4h. Synthesized materials were characterized using Fourier Transform Infrared Spectroscopy (FTIR) Shimadzu IR Prestige-21, Scanning Electron Microscope (SEM) Hitachi TM 3000, and an improvised 4-point probe. The substrate was prepared using a Cu wire attached to a circular Cu plate, and inserted in a cylindrical high density PET tube. Graphite powder was mixed with mineral oil using agate mortar and pestle. Then PANI/rGO was mixed with graphite/oil. This PANI/rGO/oil mixture was filled inside the tube and was pressed until a smooth surface was obtained. Through cyclic voltammetry (CV), the performance of PANI/rGO-mCPE (working electrode) was investigated by monitoring the anodic peaks of increasing concentrations of AA and UA (2-8 mM analyte, 0.1 M phosphate buffer at pH=7). The PANI/-mCPE was used as the working electrode, against Ag/AgCl RE and Pt auxiliary electrode. CV studies was conducted at a sweeping potential range of -0.2 to 1.0 V and a scan rate of 5 mVs⁻¹ for 3 cycles.

3. Results and discussion

FTIR spectral studies showed the characteristic peaks of PANI/rGO, and GO. The peak at 3400 cm⁻¹ of PANI/rGO was linked to N-H stretching mode. A peak corresponding to C-H plane bending on benzenoid ring was seen at 3100 cm⁻¹ for PANI/rGO. The 1750 and 1690 cm⁻¹ peaks for PANI/rGO contribute to the C=N stretching mode for imine. C=C stretching vibration for quinoid and benzenoid rings was seen at 1600 and 1400 cm⁻¹, respectively. C-N stretching mode for benzenoid ring is seen at 1150 cm⁻¹. In the fingerprint region, C-H plane bending vibration formed during protonation can be seen at 700 cm⁻¹ for PANI/rGO. It can be seen that the strong and broad absorption peak at 3200 cm⁻¹ corresponds to alcohol. CO₂ corresponds to the peak at 2360 cm⁻¹. The C=O stretching vibration was attributed at 1700 cm⁻¹ and C=C plane vibration is at 1600 cm⁻¹. Via **cyclic voltammetric analyses**, 2 anodic peaks were seen which correspond to mixed solutions of AA, and UA. The first anodic peak at the potential range of 0.1 to 0.3 V corresponds to ascorbic acid while the second anodic peak at 0.4 to 0.6 V confirms the presence of uric acid. **SEM morphological analyses** revealed that PANI has a porous, spongy-like structure which indicates high surface area, while rGO exhibits a wrinkled structure with aggregated sheets. When PANI and rGO are incorporated together, enhanced surface area was observed. Furthermore, **conductivity** increased by nearly nine-hundred folds, *i.e.*, 2.17x10⁻⁵S cm⁻¹ for

PANI and 2.16x10⁻⁴S cm⁻¹ for PANI/rGO. As probed via **cyclic voltammetric analyses**, the redox capability of synthesized electrodes was found to show an increasing trend of CPE < PANI-mCPE < PANI/rGO-mCPE. The **figures of merit** of the fabricated PANI/rGO-mCPE, when exposed to mixed solutions of AA and UA, are summarized in *Tab. 1*.

Tab. 1: Summary of sensors' performance towards multi-detected AA and UA (n=3).

Figures of merits	PANI/rGO-mCPE exposed to AA	PANI/rGO-mCPE exposed to UA
Sensitivity (m), μ A/mM	16.67	9.490
Linearity (r)	0.9977	0.9826
Linear working range, mM	2-8	2-8
Limit of detection, mM	1	1
Response time, s	59	115
Repeatability, %RSD	3.63	7.21

Conclusion

Combining PANI and rGO, through *in situ* chemical oxidative polymerization, resulted to higher electrical conductivity, and increased surface area, which effectively enhanced the performance of the sensor in the simultaneous detection of ascorbic acid and uric acid.

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