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Electrochemical Detection of Uric Acid on Exfoliated Nanosheets of Graphitic-Like Carbon Nitride ($g\text{-C}_3\text{N}_4$) Based Sensor

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A highly sensitive, selective and stable electrochemical sensor for detection of uric acid (UA) in aqueous solution has been successfully developed by deposition of exfoliated graphitic-like carbon nitride ($g\text{-C}_3\text{N}_4$) nanosheets on glassy carbon electrode (GCE). The synthesized $g\text{-C}_3\text{N}_4$ was confirmed by X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) and Raman spectroscopies. Field-emission scanning electron microscopy (FE-SEM) and High-resolution transmission electron microscopy (HR-TEM) were used to investigate the crystalline structure of $g\text{-C}_3\text{N}_4$. The elemental composition was characterized by energy-dispersive X-ray spectroscopy (EDXS). Compared to bare GCE, exfoliated $g\text{-C}_3\text{N}_4$ nanosheets (NS) modified GCE exhibited higher catalytic current for UA electro-oxidation at reduced over potential in 0.1 M phosphate buffered saline solution (PBS), which is essential to discriminate interfering analytes. $g\text{-C}_3\text{N}_4$ NS modified GCE showed a linear relationship between the electrochemical signal and the UA concentration from 100 to 1000 μM with fast response by differential pulse voltammetry (DPV). The common interferent molecules such as dopamine, ascorbic acid, folic acid, paracetamol, lactic acid, oxalic acid, cysteine, and ciprofloxacin were tested in 0.1 M PBS for the $g\text{-C}_3\text{N}_4$ NS modified GCE. It was found that these molecules did not affect the oxidation current of UA when they co-existed in the same buffer solution. Moreover, the modified sensor probe was tested for UA in urine samples with satisfactory recovery values. The proposed sensor offers high accuracy, sensitivity, simple fabrication and low cost. We suggest that $g\text{-C}_3\text{N}_4$ NS based sensor can be useful for UA analysis in medical, environmental, food and industrial applications.

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Uric acid (UA) is found to have great significance in the physiology functions of living organisms and is involved in numerous biological processes.^{1,2} Serum UA is the primary water-insoluble end product of purine metabolism in the human body and it is an important biomolecule present in urine and blood.^{3,4} Excessive, unusually low, or highly time-variable UA concentration is associated with clinical disorders such as gout, pneumonia, type 2 diabetes, leukemia, toxemia during pregnancy, chronic renal disease, multiple sclerosis, hypertension and metabolic disorders.⁵⁻¹⁰ A simple and low cost method for determination of UA concentration would be useful since UA serves as a marker for the diagnosis of above conditions. Various standard analytical methods have been developed to determine UA such as high performance liquid chromatography (HPLC), a potentiometric enzyme electrode, flow-injection analysis, amperometry *etc.*¹¹⁻¹⁶ These methods have some drawbacks such as high cost, tedious sample preparation, slow measurement, unsuitability for use outside of a laboratory setting, and requirement to be performed by skilled technicians. Among these options, electrochemical sensors (ECS) are attractive for detection of bio-molecules which exhibit electrochemical activity. ECS offers high accuracy with sensitivity, no interference, fast analysis, is user friendly and is low-cost. In order to prepare ECS, various modification strategies have been reported using bare electrodes coated with nanomaterials/electrocatalysts as the redox dynamic site.^{8,17-20}

Carbon materials such as graphene oxide (GO), carbon nanotubes (CNTs), carbon microspheres (CMP), and carbon quantum dots (CQDs) have been used for UA detection due to their excellent electrocatalytic properties.²¹⁻²⁴ These carbon materials have some limitations such as difficulty of integration, low specific surface area and poor durability. As an emerging alternative, 2D graphitic-like carbon nitride ($g\text{-C}_3\text{N}_4$) is a fascinating example of a metal-free semiconductor material with a stacked 2D structure.²⁵⁻²⁷

Recently, $g\text{-C}_3\text{N}_4$ has attracted much attention because of its remarkable structure, consisting of mainly covalent bonding of carbon

and nitrogen by a π -conjugated polymeric network. $g\text{-C}_3\text{N}_4$ is two dimensional semiconducting, layered, metal-free, easily synthesizable, nontoxic, and a biocompatible material. It is the most stable allotrope of carbon nitride with high chemical and thermal stability. $g\text{-C}_3\text{N}_4$ provides more active reaction sites (large surface area) for electron donor/acceptors with tunable electronic structure. Because of these extraordinary properties, $g\text{-C}_3\text{N}_4$ has been utilized in the fields of catalysis and sensing.²⁸⁻³¹

It is worth to mention that as synthesized bulk $g\text{-C}_3\text{N}_4$ has poor conductivity, poor water solubility, and large particle size (low specific area), so that it is not suitable for electrochemical applications. In order to be well-utilized in the field of the sensor design, it is necessary to do further exfoliation of bulk $g\text{-C}_3\text{N}_4$ to nanosheets (NS). The exfoliated ultrathin $g\text{-C}_3\text{N}_4$ NS have higher specific surface area and provide more surface-active sites. More importantly, reports have demonstrated that the ultrathin $g\text{-C}_3\text{N}_4$ NS have better electrochemical activity and stability than bulk $g\text{-C}_3\text{N}_4$; this suggests that exfoliated ultrathin $g\text{-C}_3\text{N}_4$ NS are a promising candidate material for electrochemical applications.³²⁻³⁸

Electrochemical detection methods of UA were reported by both enzymatic and non-enzymatic approaches.^{39,40} Major drawbacks associated with enzymatic sensors include difficulties associated with enzyme immobilization on the electrode surface, limited working conditions such as humidity, pH, temperature, denaturing, lack of reproducibility and high cost.⁴¹ Nevertheless, two-dimensional (2D) nanomaterials with unique structure and physicochemical properties, have gained wide attention in electrochemical applications for sensors, energy storage and conversion.⁴² Various 2D materials based sensors have also been developed for UA detection using rGO-ZnO,⁴³ Au-rGO,¹¹ Pdop@GR/MWCNTs,⁴⁴ rGO-PAMAM-MWCNT-AuNP,⁴⁵ MoS₂-PEDOT/GCE,⁴⁶ PtNi/MoS₂,⁴⁷ MoS₂-AuNP⁴⁸ and MoS₂.⁴² These materials have some limitations such as tedious synthesis process, nanosheets easily aggregate and showed poor conductivity, relatively expensive, *etc.*⁴⁹ Therefore, their application as electrocatalytic active material was limited for the detection of the small biomolecules.⁵⁰ Thus, there is a demand for developing a simple sensor which can detect UA with high sensitivity and selectivity at relatively low cost.

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Figure 1. Condensation reaction of melamine to give discrete oligomers, polymers and extended networks.

Herein, we demonstrated a novel and highly sensitive electrochemical sensor for UA detection using a glassy carbon electrode (GCE) modified with exfoliated ultrathin g-C₃N₄ NS. The exfoliated g-C₃N₄ NS were comprehensively characterized by various techniques. X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) and Raman spectroscopies were used to analyze crystalline structure and functional groups of g-C₃N₄, respectively. Surface morphology and the crystalline nature were investigated by using Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The elemental and chemical compositions were characterized by Energy-dispersive X-ray spectroscopy (EDXS). Furthermore, the electrochemical properties of g-C₃N₄ NS/GCE were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The new g-C₃N₄ NS probe exhibited a wide linear response over the concentration range from 100 to 1000 μ M UA. Furthermore, detection of UA in a human urine sample is demonstrated with high accuracy. This new sensor offers high accuracy with sensitivity, no interferent effect, fast analysis, is user friendly, non-enzymatic and is low-cost.

Experimental

Materials.—All the chemicals and reagents (Melamine, dopamine, uric acid, ascorbic acid, folic acid, paracetamol, lactic acid, oxalic acid, cysteine and ciprofloxacin) were purchased from Sigma-Aldrich and Alfa Aesar, India. They were of analytical grade and used without further purification. The required solutions were prepared with ultrapure deionized water (Millipore water purification system).

Synthesis of bulk g-C₃N₄.—Bulk g-C₃N₄ was prepared by a direct decomposition method. One gram of melamine was placed on a ceramic quartz boat crucible and heated at a rate of 5°C min^{−1} to 550°C in a tubular furnace and then maintained at this temperature (550°C) for 3 h under an atmospheric environment. The crucible was then cooled to room temperature, and the light-yellow colored g-C₃N₄ product was collected and grinded into a powder for further use. Synthesized g-C₃N₄ powder is referred as bulk g-C₃N₄. Fig. 1 shows schematically the formation process of g-C₃N₄ from melamine. The condensation reaction of melamine results in discrete oligomers which converted to polymers and extended networks. The graphitic planes are constructed from tri-s-triazine units connected by planar amino groups.⁵¹

Synthesis of exfoliated g-C₃N₄ nanosheets (NS).—Bulk g-C₃N₄ powder (0.2 g) was dispersed in 50 mL of ultrapure deionized water and then subjected to ultrasonication (probe-assisted) for 2 h (50%

amplitude, pulsed for 3 seconds on and 2 seconds off). After ultrasonication, the solution was allowed to stand undisturbed for 3 h at room temperature to allow unexfoliated bulk g-C₃N₄ particles to settle at the bottom of the container. The supernatant liquid (a homogenized dispersion) of exfoliated g-C₃N₄ NS was collected and used for further studies (Fig. 2. (a) Bulk g-C₃N₄ powder and (b) exfoliated g-C₃N₄ NS dispersion).

Preparation of exfoliated g-C₃N₄ NS modified GCE.—The bare GCE with a diameter of 3 mm was polished on a polishing cloth pad with alumina slurry (with varied particle sizes from 1.0, 0.3 and 0.05 μ m) and then successively rinsed with distilled water and ethanol several times. Finally, it was cleaned by placing the electrode in water-ethanol solution for two min under bath sonication. Then, 10 μ L exfoliated g-C₃N₄ NS dispersion was drop-casted on the cleaned GCE surface and dried overnight at room temperature. The prepared

Figure 2. Visual appearance of (a) bulk g-C₃N₄ and (b) exfoliated g-C₃N₄ NS.

Scheme 1. Schematic representation of sensor fabrication and UA oxidation process at g-C₃N₄ NS modified GCE.

electrode is hereinafter referred to as “exfoliated g-C₃N₄ NS modified GCE (g-C₃N₄ NS/GCE).” This g-C₃N₄ NS/GCE was used for further characterization and applications (Scheme 1).

Materials characterization.—The functional groups of bulk g-C₃N₄ were characterized by FT-IR (Nicolet Impact 400 D spectrometer) in the wavenumber range of 4000–400 cm^{−1}. The crystal structure and phase composition of g-C₃N₄ were measured by using a powder X-ray diffraction spectrometer (X’pert powder XRD system, Malvern Panalytical) in the 2θ range of 20° to 100° with Cu Kα radiation (λ = 0.15406 nm). Raman spectroscopy was performed at ambient conditions with 633 nm laser excitation (LabRAM HR evolution, Horiba). The surface morphology of the samples was investigated using FE-SEM (SEM 7500F, Jeol) at an accelerating voltage 20 kV. A transmission electron microscope (TEM, JEM-2100 Plus, Jeol) operating at 200 kV and capable of Energy-dispersive X-ray spectroscopy (EDXS) was employed for surface, elemental and chemical composition analysis.

Electrochemical measurements.—CV and DPV were carried out in a conventional three electrode cell setup using a CHI 760 E electro-

chemical workstation. 0.1 M phosphate buffered saline (PBS) solution was used as supporting electrolyte at room temperature (25 ± 2°C). Platinum wire, exfoliated g-C₃N₄ NS modified GCE and Ag/AgCl (3 M KCl) were used as counter, working and reference electrodes, respectively.

Spiked sample analysis.—A human urine sample was collected from a healthy volunteer (male, 22 years old). After the collection, urine was promptly refrigerated. The originally collected urine sample (10 μL) (without any additional pretreatment process) was added into 10 mL of 0.1 M PBS (pH 7.4) for the electrochemical measurements. Furthermore, known concentrations of UA (100 μM, 200 μM and 300 μM) were spiked into the above PBS (containing urine sample) and DPVs were recorded. The recoveries of the spiked UA concentrations were evaluated and ranged between 99.6 to 101.5%.⁵²

Results and Discussion

FT-IR spectrum.—FT-IR spectrum was recorded to determine the surface functional groups present on the prepared bulk g-C₃N₄. Fig. 3a exhibits a broad band at 3292 cm^{−1} which can be attributed to the

Figure 3. (a) FT-IR spectrum and (b) XRD pattern of synthesized bulk g-C₃N₄.

Figure 4. Raman spectrum of bulk g-C₃N₄ (with 633 nm excitation).

stretching vibration modes of the NH₂ or N–H groups.⁵³ The peaks at 1242 cm^{−1}, 1325 cm^{−1}, 1423 cm^{−1}, 1560 cm^{−1} and 1642 cm^{−1} correspond to the typical stretching vibration modes of C = N and C–N heterocycles.⁵⁴ The small peak located at 806 cm^{−1} is a signature of the characteristic breathing vibration mode of the triazine rings present in g-C₃N₄. The absorption feature at 889 cm^{−1} was associated to a deformation mode of cross-linked heptazine. All the characteristic peaks were in good agreement with the earlier reports of synthesized g-C₃N₄.⁵⁵

XRD and Raman analysis.—The powder XRD pattern of as-synthesized bulk g-C₃N₄ is shown in Fig. 3b. The strong peak at 27.62° was assigned to the (002) plane interlayer stacking of the conjugated aromatic ring system of g-C₃N₄. This characteristic peak is in good agreement with prior reports on synthesized g-C₃N₄.^{56,57} Furthermore, Fig. 4 shows the Raman spectrum of synthesized bulk g-C₃N₄ with several characteristic bands observed at 1579, 1482, 1149, 985, 705 and 473 cm^{−1} corresponding to the typical vibration modes of C–N and C=N heterocycles.^{58,59}

FE-SEM, TEM and EDXS analysis.—The surface morphology of the synthesized bulk g-C₃N₄ is recorded by FE-SEM as shown in Fig. 5a, which revealed the presences of agglomerated particles with average sizes of ~0.5 to 1 μm. Fig. 5b shows the TEM images of the exfoliated g-C₃N₄ NS, where we could observe several flat layered like sheets with the dimension of ~10 nm. Inset of Fig. 5b is a HR-TEM image of g-C₃N₄ NS with a lattice fringe spacing of 0.324 nm which corresponded to the (002) crystal plane of g-C₃N₄ (JCPDS 87-1526). The elemental mapping (EDXS spectrum) of the sample is also revealed the presence of high intensity bands of C and N, which indicated the successful synthesis of g-C₃N₄ nanosheets (Fig. 5c). The crystalline nature of g-C₃N₄ nanosheets is also characterized by a SAED pattern (Fig. 5d). The SAED pattern revealed that bright continuous concentric rings attributed to diffraction from the 002 planes of g-C₃N₄ and is consistent with the XRD data. We also estimated the average film thickness of the g-C₃N₄ nanosheets on the electrode surface. For this purpose, 10 μL of g-C₃N₄ NS dispersion was drop-casted on Cu grid and analyzed by TEM. Using the obtained TEM image, the approximate film thickness of g-C₃N₄ NS film was estimated to be around ~0.1 μm (Fig. 5b).

Electrochemical oxidation of UA at g-C₃N₄ NS modified GCE.—Electrochemical oxidation of 1 mM UA was tested on a bare GCE and g-C₃N₄ NS modified GCE (at a scan rate of 50 mV s^{−1} in 0.1 M

Figure 5. (a) SEM images of the synthesized bulk g-C₃N₄, (b) TEM images of exfoliated g-C₃N₄ NS and the inset shows the HR-TEM image of the g-C₃N₄ NS film from which the lattice fringes can be clearly seen. (c) EDX spectrum of g-C₃N₄ NS and (d) selected area electron diffraction (SAED) pattern of g-C₃N₄.

PBS, pH 7.4) in the potential range of 0 to 1 V as shown in Fig. 6. The g-C₃N₄ NS modified GCE exhibited a highly enhanced oxidation peak centered at 0.45 V (red curve). Whereas, UA oxidation at the bare GCE showed a lower oxidation peak current at higher positive potential (0.53 V) (black curve). It was obvious that modified g-C₃N₄ NS/GCE produced highly enhanced catalytic current of UA oxidation compared to the bare GCE. This establishes that g-C₃N₄ NS exhibit high electro-catalytic activity useful for UA sensing. In addition, the UA oxidation peak was shifted to a lower potential than that of the unmodified electrode. These data indicated that electrode surface modification with g-C₃N₄ NS improves the electrocatalytic UA oxidation process. A possible reaction mechanism for the oxidation of UA at the

Figure 6. CVs of bare GCE (black curve) and g-C₃N₄ NS modified GCE (red curve) recorded with 1 mM UA in 0.1 M PBS (pH 7.4) (Scan rate = 50 mV s^{−1}). (Inset: photographic images of g-C₃N₄ NS modified GCE sensor).

Figure 7. Schematic representation of UA electro-oxidation mechanism at the exfoliated g-C₃N₄ NS modified GCE surface.

g-C₃N₄ NS modified GCE is illustrated in Fig. 7. As UA oxidation is a two-electron transfer process, uric acid (1H-purine-2,6,8(3H,7H,9H)-trione) is converted into (1H-purine-2,6,8(9H)-trione).^{60,61} Hence, the electrochemical oxidation of UA on modified GCE takes place by direct transfer of two protons and two electrons by a chemical conversion. The effect of scan rate (ν) on UA oxidation peak current (I_{pa}) was investigated at g-C₃N₄ NS/GCE by using cyclic voltammetry in 0.1 M PBS solution.

Fig. 8a shows cyclic voltammograms (CVs) of the g-C₃N₄ NS/GCE in 1 mM UA at different scan rates from 10 to 100 mV s⁻¹. According to the Randles-Sevcik formula (Equation 1),⁶² it can be clearly seen that the I_{pa} increases against square roots of scan rate with a linear correlation coefficient of (R^2) 0.9659 (Fig. 8b).

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C \nu^{1/2} \quad [1]$$

Where I_p is the oxidation peak current (A), n is the number of transferred electrons per mole, A is the active surface area of the electrode (cm²), D is the diffusion coefficient (cm²/sec), C is concentration (mol/cm³) and ν is the scan rate (V/s). These results indicated that the oxidation of UA on g-C₃N₄ NS/GCE is a diffusion-controlled electrochemical processes (Fig. 8b).⁶³

Determination of UA by DPV.—DPV is a highly sensitive technique that has been commonly used for electrochemical detection. Fig. 9a shows the DPV curves of different concentrations for UA on g-C₃N₄ NS modified GCE. As we recorded, the electro-catalytic oxidation peak current of UA increases linearly with concentration from 100 to 1000 μ M. Fig. 9b shows a good linear relationship between

the concentrations and the peak currents with a linear correlation coefficient of (R^2) 0.9960. This proved that the electro-catalytic oxidation of UA at the surface of the g-C₃N₄ NS/GCE is highly sensitive and dependent on the UA concentration. We have also recorded three replicate measurements and the results were reproducible. Previously, various nanomaterials have been synthesized to prepare electrochemical sensors for the detection of UA.^{44,64–69} We have also compared our analytical data with some of other reported methods for electrochemical detection of UA in Table I. This proposed new method offers a number of advantages. For example, the demonstrated concentration range over which our detector response is linear from 100 μ M –1000 μ M compares well with the other reported methods. It also exhibits better selectivity and lower limit of detection (LOD) for UA (Table I). The LOD was calculated using the following Equation 2:

$$\text{LOD} = 3\sigma_B/S \quad [2]$$

Where σ_B is the standard deviation of the current measured on a blank sample (9.0×10^{-8} A) and S is the slope of the calibration curve (2.025×10^{-8} A μ M⁻¹). The calculated LOD value was 4.45 μ M which was better than some of the reported UA sensors (Table I).

Determination of UA in a spiked sample.—The proposed sensor was applied to detect UA in a spiked sample (as given in Spiked sample analysis section). As shown in Fig. 10, after each addition of UA, peak currents were increased at g-C₃N₄ NS/GCE due to catalytic oxidation of UA (Note: UA concentration in original urine sample was not determined). The known concentrations of UA (For example: 100

Figure 8. (a) CVs were recorded using g-C₃N₄ NS modified GCE in 0.1 M PBS (pH 7.4) with 1 mM UA at different scan rates. (b) Linear plot of I_{pa} of UA vs. (scan rate)^{1/2}.

Figure 9. (a) DPVs of g-C₃N₄ NS modified GCE recorded over UA concentrations range from 100 μM to 1000 μM. (b) Calibration curve of UA (I_{pa} vs. [UA]).

Figure 10. DPVs of g-C₃N₄ NS modified GCE recorded in 0.1 M PBS with urine sample spiked with 100, 200 and 300 μM UA.

μM, 200 μM and 300 μM) were spiked into PBS containing human urine sample and analyzed by this g-C₃N₄ NS/GCE sensor to validate its suitability for practical applications.⁷⁰ The recovery results (using Eq. 3) are provided in Table II. It indicated that this new sensor can be applied for accurate measurement of UA in real samples.

$$\text{Recovery (\%)} = C_{\text{found}}/C_{\text{spiked}} \times 100 \quad [3]$$

Interference and selectivity studies.—The selectivity of the g-C₃N₄ NS/GCE sensor for UA over possible interfering molecules is an essential requirement in electro-analysis. We have recorded DPV in the absence and presence of various other molecules to investigate selectivity of the proposed sensor. Molecules such as dopamine (0.5 mM, DA), ascorbic acid (1 mM, AA), folic acid (0.5 mM, FA), paracetamol (0.5 mM, PA), lactic acid (0.5 mM, LA), oxalic acid (0.5 mM, OA), cysteine (Cy) (0.5 mM), and ciprofloxacin (Cip) (0.5 mM) were investigated in 0.1 M PBS. These molecules did not affect the oxidation current of UA when they co-existed in the same buffer solution. Only negligible current (signal change < 6.0% decreased) changes were observed as shown in Fig. 11. These results suggested that UA detection on g-C₃N₄ NS/GCE sensor is highly selective without any

Table I. Analytical comparison of linear range and LODs of other modified electrodes reported for electrochemical detection of UA.

Catalytic Material*	Electrode	Electrochemical Method	Detection range (μM)	LOD (μM)	Refs.
Pt/PAAQ	GCE	DPV	35–420	11.5	64
PMMA	GCE	DPV	20–170	6.38	65
PrGO/PB 100	GCE	CV	40–415	8.0	66
HNP-PtTi	GCE	DPV	100–1000	5.3	67
Pd/CNFsc	GCE	DPV	50–4000	15	4
Pdop@GR/MWCNTs	GCE	DPV	20.0–320.0	15	44
Trp-GR/GCE	GCE	DPV	10–1000	12.9	68
Pyrolytic graphite electrode	PGE	DPV	21–336	21	70
MWCNT/PEDOT film	GCE	DPV	10–250	10	69
g-C ₃ N ₄ NS	GCE	DPV	100–1000	4.45	This work

*Footnotes:

Poly (1-aminoanthraquinone) (PAAQ),
 Polymethylmethacrylate (PMMA),
 Photochemically reduced graphene oxide/Prussian blue (PrGO/PB),
 Hierarchical nanoporous (HNP),
 Palladium/carbon nanofibers (Pd/CNFsc),
 Polydopamine (Pdop), graphene (GR) and multiwalled carbon nanotubes (MWCNTs).
 Tryptophan-functionalized graphene (Trp-GR).
 Multi-walled carbon nanotubes-poly(3,4-ethylenedioxythiophene) (MWCNT/PEDOT).

Table II. Electrochemical detection of UA spiked in urine samples using g-C₃N₄ NS modified GCE as a sensor.

Added (μM)	Found (μM)	Recovery (%)	RSD ^a (%)
100	99.6	99.6	1.92
200	202	101	2.36
300	304	101.3	2.24

^aThree number of measurements carried out ($n = 3$).

significant interference effects. Previously, g-C₃N₄ NS with graphene oxide based composite coated electrode was prepared and reported for simultaneous detection AA, DA and UA in pH 4.0.³⁸ In that work, it was mentioned that GO provided a selective interface for effective oxidation of these molecules, not g-C₃N₄. In addition, g-C₃N₄ was used to enhance the electrical properties of the composite.³⁸ In contrast, in this work, exfoliated g-C₃N₄ NS (single component) was tested and found that it could be useful for selective detection of UA at pH 7.4. However, further studies may be required to understand the selectivity of g-C₃N₄ NS for UA oxidation.

Conclusions

In summary, we have developed a new electrochemical sensor using exfoliated ultrathin g-C₃N₄ NS as an effective electrocatalyst for highly sensitive measurement of UA. FT-IR, XRD, Raman spectroscopy, FE-SEM, HR-TEM, and EDXS confirmed the successful synthesis of g-C₃N₄. Moreover, the material was demonstrated to be an efficient electrocatalyst for UA and showed a fast response, wide linear range of detection (100 to 1000 μM) with high sensitivity and selectivity. In addition, g-C₃N₄ NS had anti-interference ability in the presence of other biomolecules. Finally, the developed g-C₃N₄ NS based sensor was used to detect spiked UA in human urine samples with high accuracy. This sensor also offers several advantages such as easy fabrication, it is simple to operate, is highly sensitive and selective, with low cost for UA detection. We conclude that this new sensor may be suitable for UA analysis in various environmental, medical, food and industrial samples.

Figure 11. DPVs recorded for the interferent molecules on g-C₃N₄ NS/GCE for the successive additions of 0.5 mM DA, 1 mM AA, 0.5 mM FA, 0.5 mM PA, 0.5 mM LA, 0.5 mM OA, 0.5 mM cysteine and 0.5 mM ciprofloxacin with 1 mM UA in 0.1 M PBS (pH 7.4).

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Reference

- C.-L. Sun, H.-H. Lee, J.-M. Yang, and C.-C. Wu, *Biosensors and Bioelectronics*, **26**, 3450 (2011).
- Z.-H. Sheng, X.-Q. Zheng, J.-Y. Xu, W.-J. Bao, F.-B. Wang, and X.-H. Xia, *Biosensors and Bioelectronics*, **34**, 125 (2012).
- K. Jindal, M. Tomar, and V. Gupta, *Analyst*, **138**, 4353 (2013).
- J. Huang, Y. Liu, H. Hou, and T. You, *Biosensors and Bioelectronics*, **24**, 632 (2008).
- S. A. Kumar, H. W. Cheng, and S. M. Chen, *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis*, **21**, 2281 (2009).
- L. Yang, D. Liu, J. Huang, and T. You, *Sensors and Actuators B: Chemical*, **193**, 166 (2014).
- X. Liu, L. Zhang, S. Wei, S. Chen, X. Ou, and Q. Lu, *Biosensors and Bioelectronics*, **57**, 232 (2014).
- A. Abellán-Llobregat, C. González-Gaitán, L. Vidal, A. Canals, and E. Morallon, *Biosensors and Bioelectronics*, **109**, 123 (2018).
- N. Lavanya, E. Fazio, F. Neri, A. Bonavita, S. Leonardi, G. Neri, and C. Sekar, *Sensors and Actuators B: Chemical*, **221**, 1412 (2015).
- Z. Bai, C. Zhou, H. Xu, G. Wang, H. Pang, and H. Ma, *Sensors and Actuators B: Chemical*, **243**, 361 (2017).
- C. Wang, J. Du, H. Wang, C. E. Zou, F. Jiang, P. Yang, and Y. Du, *Sensors and Actuators B: Chemical*, **204**, 302 (2014).
- X. Dai, X. Fang, C. Zhang, R. Xu, and B. Xu, *Journal of Chromatography B*, **857**, 287 (2007).
- Y. Li, G. Ran, W. J. Yi, H. Q. Luo, and N. B. Li, *Microchimica Acta*, **178**, 115 (2012).
- A. Joshi, W. Schuhmann, and T. C. Nagaiah, *Sensors and Actuators B: Chemical*, **230**, 544 (2016).
- M. B. Q. Garcia, J. Lima, M. L. Silva, and J. Sousa, *Portugaliae Electrochimica Acta*, **22**, 249 (2004).
- Y. Zhang, G. Wen, Y. Zhou, S. Shuang, C. Dong, and M. M. Choi, *Biosensors and Bioelectronics*, **22**, 1791 (2007).
- W. Zhang, Y. Chai, R. Yuan, S. Chen, J. Han, and D. Yuan, *Analytica chimica acta*, **756**, 7 (2012).
- B. Fang, Y. Feng, G. Wang, C. Zhang, A. Gu, and M. Liu, *Microchimica Acta*, **173**, 27 (2011).
- C.-L. Sun, C.-T. Chang, H.-H. Lee, J. Zhou, J. Wang, T.-K. Sham, and W.-F. Pong, *ACS Nano*, **5**, 7788 (2011).
- T. V. Kumar and A. K. Sundramoorthy, *Journal of The Electrochemical Society*, **165**, B3006 (2018).
- D. Yuan, S. Chen, R. Yuan, J. Zhang, and X. Liu, *Sensors and Actuators B: Chemical*, **191**, 415 (2014).
- C. Deng, J. Chen, M. Wang, C. Xiao, Z. Nie, and S. Yao, *Biosensors and Bioelectronics*, **24**, 2091 (2009).
- D. Jia, J. Dai, H. Yuan, L. Lei, and D. Xiao, *Talanta*, **85**, 2344 (2011).
- Q. Lu, J. Zhang, X. Liu, Y. Wu, R. Yuan, and S. Chen, *Analyst*, **139**, 6556 (2014).
- Z. Mao, J. Chen, Y. Yang, D. Wang, L. Bie, and B. D. Fahlman, *ACS applied materials & interfaces*, **9**, 12427 (2017).
- J. Xu and M. Antonietti, *Journal of the American Chemical Society*, **139**, 6026 (2017).
- M. Groenewolt and M. Antonietti, *Advanced materials*, **17**, 1789 (2005).
- J. Tian, Q. Liu, C. Ge, Z. Xing, A. M. Asiri, A. O. Al-Youbi, and X. Sun, *Nanoscale*, **5**, 8921 (2013).
- P. Chen, F. Wang, Q. Zhang, Y. Su, L. Shen, K. Yao, Z.-F. Chen, Y. Liu, Z. Cai, and W. Lv, *Chemosphere*, **172**, 193 (2017).
- G. Shiravand, A. Badiie, and G. M. Ziarani, *Sensors and Actuators B: Chemical*, **242**, 244 (2017).
- F. Zhao, H. Cheng, Y. Hu, L. Song, Z. Zhang, L. Jiang, and L. Qu, *Scientific reports*, **4**, 5882 (2014).
- X. Zhang, X. Xie, H. Wang, J. Zhang, B. Pan, and Y. Xie, *Journal of the American Chemical Society*, **135**, 18 (2012).
- X. Dong and F. Cheng, *Journal of Materials Chemistry A*, **3**, 23642 (2015).
- J. Tian, Q. Liu, A. M. Asiri, A. H. Qusti, A. O. Al-Youbi, and X. Sun, *Nanoscale*, **5**, 11604 (2013).
- H. Xu, J. Yan, X. She, L. Xu, J. Xia, Y. Xu, Y. Song, L. Huang, and H. Li, *Nanoscale*, **6**, 1406 (2014).
- P. Niu, L. Zhang, G. Liu, and H. M. Cheng, *Advanced Functional Materials*, **22**, 4763 (2012).
- H. Gu, T. Zhou, and G. Shi, *Talanta*, **132**, 871 (2015).

38. H. Zhang, Q. Huang, Y. Huang, F. Li, W. Zhang, C. Wei, J. Chen, P. Dai, L. Huang, and Z. Huang, *Electrochimica Acta*, **142**, 125 (2014).
39. K. Arora, M. Tomar, and V. Gupta, *Analyst*, **139**, 837 (2014).
40. J. Wang, B. Yang, J. Zhong, B. Yan, K. Zhang, C. Zhai, Y. Shiraishi, Y. Du, and P. Yang, *Journal of colloid and interface science*, **497**, 172 (2017).
41. M. B. Wayu, M. A. Schwarzmann, S. D. Gillespie, and M. C. Leopold, *Journal of materials science*, **52**, 6050 (2017).
42. R. Sha, N. Vishnu, and S. Badhulika, *Sensors and Actuators B: Chemical*, **279**, 53 (2019).
43. X. Zhang, Y.-C. Zhang, and L.-X. Ma, *Sensors and Actuators B: Chemical*, **227**, 488 (2016).
44. C. Wang, J. Li, K. Shi, Q. Wang, X. Zhao, Z. Xiong, X. Zou, and Y. Wang, *Journal of Electroanalytical Chemistry*, **770**, 56 (2016).
45. S. Wang, W. Zhang, X. Zhong, Y. Chai, and R. Yuan, *Analytical Methods*, **7**, 1471 (2015).
46. Y. Li, H. Lin, H. Peng, R. Qi, and C. Luo, *Microchimica Acta*, **183**, 2517 (2016).
47. L. Ma, Q. Zhang, C. Wu, Y. Zhang, and L. Zeng, *Analytica chimica acta*, **1055**, 17 (2019).
48. H. Sun, J. Chao, X. Zuo, S. Su, X. Liu, L. Yuwen, C. Fan, and L. Wang, *Rsc Advances*, **4**, 27625 (2014).
49. B. Xu, B. Zhang, L. Yang, F. Zhao, and B. Zeng, *Electrochimica Acta*, **258**, 1413 (2017).
50. L. Lu, *Biosensors and Bioelectronics*, **110**, 180 (2018).
51. A. Wang, C. Wang, L. Fu, W. Wong-Ng, and Y. Lan, *Nano-micro letters*, **9**, 47 (2017).
52. H. Beitollahi, F. G. Nejad, and S. Shakeri, *Analytical Methods*, **9**, 5541 (2017).
53. F. Jiang, T. Yan, H. Chen, A. Sun, C. Xu, and X. Wang, *Applied Surface Science*, **295**, 164 (2014).
54. T. Di, B. Zhu, B. Cheng, J. Yu, and J. Xu, *Journal of Catalysis*, **352**, 532 (2017).
55. P. Xia, B. Zhu, B. Cheng, J. Yu, and J. Xu, *ACS Sustainable Chemistry & Engineering*, **6**, 965 (2017).
56. Q. Y. Shan, B. Guan, S. J. Zhu, H. J. Zhang, and Y. X. Zhang, *RSC Advances*, **6**, 83209 (2016).
57. X. Bai, R. Zong, C. Li, D. Liu, Y. Liu, and Y. Zhu, *Applied Catalysis B: Environmental*, **147**, 82 (2014).
58. J. Ma, C. Wang, and H. He, *Applied Catalysis B: Environmental*, **184**, 28 (2016).
59. D. Zeng, W.-J. Ong, H. Zheng, M. Wu, Y. Chen, D.-L. Peng, and M.-Y. Han, *Journal of Materials Chemistry A*, **5**, 16171 (2017).
60. N. Tukimin, J. Abdullah, and Y. Sulaiman, *Journal of The Electrochemical Society*, **165**, B258 (2018).
61. G. Fabregat, J. Casanovas, E. Redondo, E. Armelin, and C. Alemán, *Physical Chemistry Chemical Physics*, **16**, 7850 (2014).
62. S. Huang, S. Song, H. Yue, X. Gao, B. Wang, and E. Guo, *Sensors and Actuators B: Chemical*, **277**, 381 (2018).
63. X. Tian, C. Cheng, H. Yuan, J. Du, D. Xiao, S. Xie, and M. M. Choi, *Talanta*, **93**, 79 (2012).
64. E. de Pieri Troiani and R. C. Faria, *Journal of Applied Electrochemistry*, **43**, 919 (2013).
65. Y. Zhang, Q. Zhou, W. Zhao, W. Chu, and J. Zheng, *Electrochimica Acta*, **212**, 25 (2016).
66. P. L. dos Santos, V. Katic, K. C. Toledo, and J. A. Bonacin, *Sensors and Actuators B: Chemical*, **255**, 2437 (2018).
67. D. Zhao, G. Yu, K. Tian, and C. Xu, *Biosensors and Bioelectronics*, **82**, 119 (2016).
68. Q. Lian, Z. He, Q. He, A. Luo, K. Yan, D. Zhang, X. Lu, and X. Zhou, *Analytica chimica acta*, **823**, 32 (2014).
69. K.-C. Lin, T.-H. Tsai, and S.-M. Chen, *Biosensors and Bioelectronics*, **26**, 608 (2010).
70. R. P. da Silva, A. W. O. Lima, and S. H. Serrano, *Analytica chimica acta*, **612**, 89 (2008).