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Mesoporous Carbon Nanomaterial-Phytochemical Based Electro-active Composite Preparation and its Application for Selective Hydrazine Sensing

Khairunnisa Amreen* and M. Sujatha

Department of Chemistry-PG, St. Anns' College for Women, Mehdipatnam, Hyderabad-500028, India

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This work reports the preparation of a graphitized mesoporous carbon and a phytochemical; piperine based electro-active composite. The composite was chemically modified over a glassy carbon electrode, designated as GCE/GMC@pp. The GCE/GMC@pp exhibited a highly stable redox peak at $E_{1/2} = 0.2$ V vs. Ag/AgCl in pH 7 phosphate buffer solution (PBS). Further, the prepared electrode gave an exceptionally selective response towards Hydrazine (HyD) sensing at $E^0 = 0.235$ V vs. Ag/AgCl. In addition, the sensor gave a linear response towards the changing HyD concentration from 10-90 μ M with the limit of detection as 120 nM. To explore the practical applicability, the effect of interference with co-existing analytes like H_2O_2 , Pb^{2+} , Cd^{2+} , NO_2^{3-} , NO_2^{2-} , Cr(II), Arsenic (Ars) were studied and an interference mitigated response was observed. Finally, a real sample of tap water was tested and appreciable recovery values were obtained. Overall, the prepared composite exhibited excellent electro-catalytic activity towards HyD and has great potential for the real time trace HyD detection.

Keywords: Piperine, Mesoporous, Composite, Hydrazine, Electro-active, Sensing

INTRODUCTION

Graphitized mesoporous carbon (GMC) nanomaterial has gained significant interest in recent times. Owing to its porous, graphitic frame network, GMC proves to be an ideal carbon matrix for composite preparation [1]. With an average pore size of 2-50 nm and fewer functional groups, morphologically, GMC has added advantages over other orthodox carbon nanomaterials [2]. Macromolecules like hemoglobin [3], hematin [4], phytochemicals [5], can easily interact with these pores. In the present work, commercially available GMC is employed for the preparation of a composite with a commercial phytochemical; Piperine designated as GMC@pp. Piperine is a phytochemical present in spices like black pepper, long pepper, white pepper and is responsible for the flavor and pungency [6].

Literature reports numerous therapeutic uses of this

compound [6]. It is structurally a substituted hydrocarbon, hence, expected to be electrochemically redox in nature. Our group recently developed a piperine quantification method by isolating piperine from a natural product, long pepper-based upon the electrochemical redox activity [7]. Thus, we found that the composite GMC@pp can show electro-activity. To explore the same, a pure commercial piperine sample was procured and mixed with GMC to prepare a GMC@pp composite. This composite is chemically modified over a glassy carbon electrode (GCE) as GCE/GMC@pp. The fabricated electrode is further tested for hydrazine (HyD) electrochemical sensing.

HyD, an environmental pollutant, is widely used in various chemical and manufacturing industries. It is a highly toxic carcinogen [8], deployed in multiple industrial applications [9]. Henceforth, HyD pollution is an alarming concern. Urgent need for low cost and highly selective HyD sensors especially in low concentrations is prevailing. In this regard, several organic, inorganic, metal based, nanocomposite based, metal oxide based HyD

*Corresponding author. E-mail: khairunnisa.amreen90@gmail.com

electrochemical sensors [10-14] have been reported. Crude black pepper based electrochemical sensor for Hyd sensing was recently reported. Herein, the piperine was electrodeposited over graphitized mesoporous carbon with a hydrazine detection limit of 40 μM [15]. Since the method of electrode preparation was electrodeposition over GCE/GMC electrode here, the polymerization of piperine gave a lesser limit of detection. Furthermore, the presence of co-existing polyhydrocarbons also reduces electroactivity. Hence, in this case, a pure commercial sample with no other compounds was taken and the composite was prepared in an ex-situ manner. Henceforth, LOD obtained was better. Furthermore, the preparation of the electrode was simplified with this approach. Table 1 gives a comparative table of some of the reports of electrochemical detection of Hyd with various mediators using amperometry i-t curve. Since no reports with phytochemical are reported herein, other mediators are summarized stating the advantage of present work. In the present work, phytochemical is used, hence the green route of detection is adapted. Further, the composite formed is unique and gives appreciable LOD. Overall, it can be concluded that the commercial piperine when formed as a composite with GMC, can be used as an electrochemical sensor for Hyd. Zero interference from co-existing chemicals and real water sample analysis can also be performed with good recovery values.

EXPERIMENTAL

Chemicals and Reagents

Piperine, graphitized mesoporous carbon (GMC):

< 50 nm, hydrazine hydrate, hydrogen peroxide (H_2O_2), lead chloride (Pb^{2+}), cadmium sulphate (Cd^{2+}), sodium nitrate (NO_3^-), sodium nitrite (NO_2^-), chromium sulphate (Cr(II)), arsenic iodide (Ars) were procured from Sigma Aldrich. All other basic chemicals used were of analytical grade.

Apparatus

The experiment was conducted in a three-electrode system, using CHI 660 potentiostat, GCE/GMC@pp as a working electrode (WE), platinum wire as a counter (CE) and Ag/AgCl as a reference (RE). 10 ml of the pH 7 phosphate buffer solution (PBS) was used as an electrolyte, and cyclic voltammetry (CV) was performed in -0.5 V to 0.8 V potential window at 10 mV s^{-1} . 500 μM of Hyd was used as an analyte. Further, an amperometry i-t curve was employed for studying the effect of concentration, interference and real sample analysis.

Composite fabrication

To fabricate the composite, 5 mg of GMC and 5 mg of piperine (pp) (1:1) were dispersed in 500 μl of double distilled water and sonicated for 40 min in an ultrasonication bath. A pretreated clean glassy carbon electrode (GCE) was taken, (area 0.0707 cm^2). 5 μl of the prepared GMC@pp was drop coated on the electrode surface. It was air-dried for 20 min at room temperature. The fabricated GCE/GMC@pp was used as a working electrode.

Physico-chemical Characterization

Physico-chemical characterization of GMC@pp was carried out *via* Raman, FT-IR and UV-Vis spectroscopy using FTIR-4200 from Jasco, UV-Vis spectrophotometer

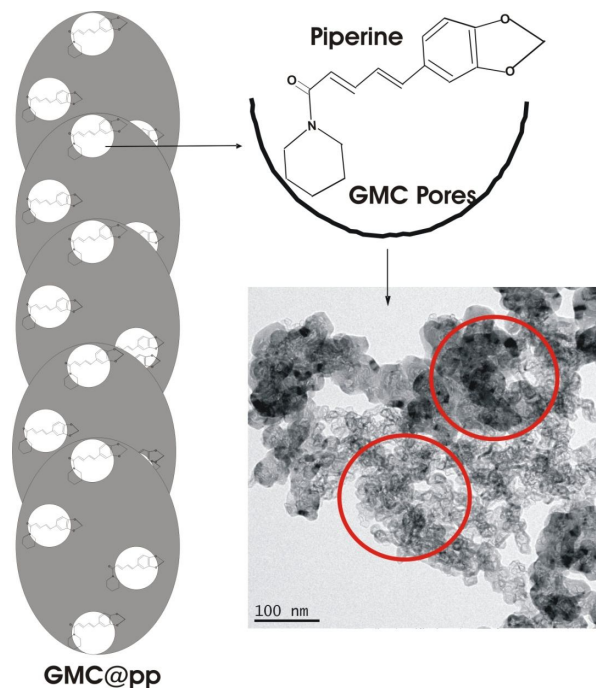
Table 1. Comparative Different Hydrazine Sensing Approaches *via* Amperometry i-t Curve

Electrode modification	Linearity (μM)	LOD (μM)	Method	Ref.
GCE/Mutliwalled carbon nanotube@carbazole	25-250	16.3	Amperometric i-t curve	[16]
GCE/Mutliwalled carbon nanotube@Ellagic acid	500-9000	0.86	Amperometric i-t curve	[17]
GCE/PEDOT/Lignosulfonate	15-290	9.8	Chronoamperometry	[18]
Pencil graphite electrode/pyrocatechol	0.2-500	0.08	Flow injection amperometry	[19]
GCE/GMC@pp	10-90	120 nM	Amperometric i-t curve	This work

V-650 JASCO, uniRAM-3300 Micro Raman Mapping spectrophotometer were used for FTIR, UV-Vis, and Raman spectroscopy. To carry out FT-IR and UV-Vis spectroscopy, the modified electrode coating was peeled out with a doctor's syringe needle. Further, the coating was added in 500 μl of the ethanol and sonicated for 10 min. This solution was filtered and was subjected to spectroscopy.

RESULTS AND DISCUSSION

Figure 1 shows a schematic representation of GMC@pp composite. Herein, it is possible that the piperine molecule might have interacted with the porous sites of GMC to form a composite. Piperine being electro-active in nature is expected to undergo an electron transfer redox mechanism aided by the GMC pores. To confirm the presence of GMC and piperine on the electrode surface, TEM characterization was taken. Spherical pores appeared masked with dark spots at multiple places. Thus, it is plausible that GMC surface has interacted with piperine to form redox active composite (Fig. 1). Furthermore, to prove the presence of piperine over GMC, physico-chemical characterization of GMC@pp was carried out *via* Raman, FT-IR and UV-Vis spectroscopy. Figure 2a, is a typical Raman spectrum, wherein, bare GMC gave D and G bands at 1275 and 1485 cm^{-1} nearer to the characteristic graphitic and distorted band [3]. Whereas, GMC@pp spectra, the band intensities were significantly changed. The calculated ID/IG ratio for bare GMC was 0.97 and GMC@pp is 1.05. This change depicts the formation of composite GMC@pp, plausible due to π - π interaction [5]. FTIR was recorded by KBr method. The electrode was coated with GMC@pp, dried, peeled off with a doctor's needle, and compressed into a pellet. Figure 2b shows comparative FTIR spectra of bare GMC wherein, no specific peak is observed implementing the absence of any functional groups. Whereas, GMC@pp gave peaks at 3280 (OH str), 2980 (C-H str), 1640 (N-H bnd), 1390 (C=C str), 1270 (C-N str), 1042 (C-O str), 877 (Ar-CH str) cm^{-1} . Hence, authenticating immobilization of piperine over GMC. Furthermore, the peaks obtained were justifiable with the structure of piperine. Figure 2c is a comparative UV-Vis spectrum. Bare GMC gave no absorbance peak; however, GMC@pp gave a peak at 340 nm. Thus, proving the composite formation.



GMC@pp
Fig. 1. Schematic representation of the GMC@pp composite modified on GCE. TEM characterization of GCE/GMC@pp.

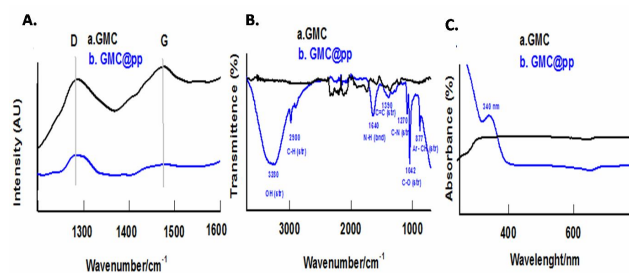


Fig. 2. Physico-chemical characterizations, (a) Raman spectrum (b) FTIR spectrum (c) UV-Vis spectrum.

The prepared composite was explored for electrochemical activity. Figure 3a is a typical comparative CV response of GCE/GMC and GCE/GMC@pp in pH 7 PBS at 50 mV s^{-1} , $n = 10$ vs. Ag/AgCl in -0.5 to 0.8 V. As can be seen, GCE/GMC@pp gave a highly stable, distinct redox peak at $E_{1/2} = 0.20$ V vs. Ag/AgCl with calculated surface excess value, $\Gamma_{pp} = 20.3 \times 10^{-9}$ $\text{mol}^{-1} \text{cm}^2$. The peak obtained was pH-independent (data not included). On the other hand, GCE/GMC failed to give any such response.

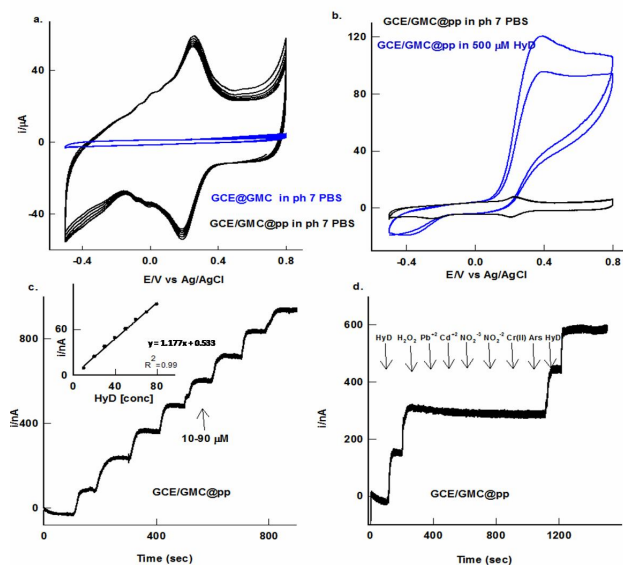


Fig. 3. (a) Comparative CV response for GCE/GMC and GCE/GMC@pp in pH 7 PBS at 50 mV s^{-1} , $n = 10$. (b) Comparative CV of GCE/GMC@pp with and without $500 \mu\text{M}$ HyD at 10 mV s^{-1} , $n = 4$. (c) A typical amperometric i-t curve response of GCE/GMC@pp with increasing HyD concentration. Inset, corresponding base line corrected calibration plot. (d) Amperometric i-t curve response of effect of various interfering analytes.

Henceforth, authenticating the electro-activity of the fabricated composite material. The chemically modified GCE with the prepared composite (GCE/GMC@pp) was stored up to 40 days and was found to be highly stable with $<2\%$ decrease in the peak current value.

Furthermore, to test the applicability of the composite as a sensor, the CV response of GCE/GMC@pp was analyzed in the presence of $500 \mu\text{M}$ HyD in pH 7PBS at 10 mV s^{-1} . Characteristic oxidation, irreversible peak at a potential $E^0 = 0.235 \text{ V}$ was obtained at 10 mV s^{-1} , $n = 4$. A similar peak was not observed in absence of HyD (in plain pH 7 PBS) (Fig. 3b). It was clearly seen that the composite could detect HyD. The mechanism of hydrazine oxidation *via* piperine has been reported earlier in our previous work [15]. In addition, the effect of varying HyD concentration was examined by the amperometric i-t curve technique. In order

to increase the sensitivity of composite material towards low HyD concentrations, this technique was adopted. A low concentration range, $10\text{-}90 \mu\text{M}$, was examined.

Figure 3c is an amperometric i-t curve stepwise response. Significant linear growth in step current was observed with each spike. Inset Fig. 3c is a corresponding baseline-corrected calibration plot which was linear with R^2 as 0.99. The calculated limit of detection was appreciable; $\text{LOD} = 120 \text{ nM}$. It was also found that the composite is highly sensitive towards low concentrations, however, through CV, a concentration as high as $500 \mu\text{M}$ also gave a significant response. To avoid the electrode fouling problem, a concentration higher than $100 \mu\text{M}$ was avoided as the fabricated composite is intended for a trace amount of HyD detection.

To analyze the selectivity and sensitivity of GCE/GMC@pp before real time application, the effect of common co-existing analytes on HyD sensing was examined. $200 \mu\text{M}$ of each interfering analyte, H_2O_2 , Pb^{2+} , Cd^{2+} , NO_3^- , NO_2^- , Cr(II) , Ars was spiked and amperometric i-t curve response was observed. There was no change in the current signal upon the addition of these analytes. However, when HyD was spiked, a significant step rise of current was observed. Thus, GCE/GMC@pp was found to be highly selective towards HyD even in the presence of a high concentration of interfering analytes and gave interference mitigated response.

In addition, as a prototype real-time application, detection of HyD in tap water was attempted *via* the standard addition approach. Known amounts of standard HyD, $10, 20, 30 \mu\text{M}$ was spiked in 5 ml tap water and 5 ml pH PBS solution and amperometric i-t curve response was studied (data not included). Table 2 summarizes the real sample analysis wherein, appreciable recovery values were obtained.

Table 2. Real Sample Analysis

Real sample	Added (μM)	Found (μM)	Recovery (%)
Tap water	10	11.2	89.2
	20	19.6	102
	30	31.0	97

CONCLUSIONS

Overall, in conclusion, a highly stable redox electro-active graphitized mesoporous carbon and piperine composite (GCE@pp) was prepared. Further, this composite was chemically modified on a glassy carbon electrode to fabricate GCE/GMC@pp. The modified electrode gave a stable redox response at $E_{1/2} = 0.20$ V vs. Ag/AgCl at 50 mV s^{-1} with a calculated surface excess value, $\Gamma_{pp} = 20.3 \times 10^{-9} \text{ mol}^{-1} \text{ cm}^2$. In addition, GCE/GMC@pp was found sensitive towards HyD giving an oxidation peak at $E^0 = 0.235$ V. The LOD was 120 nM, with no interference from co-existing analytes. As a real-time, application prototype, tap water was examined via the standard addition approach and gave appreciable recovery values. Overall, the prepared composite could be highly useful for detecting low concentrations of HyD in real samples.

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Conflict of Interest

No conflicts to declare.

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