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A simple synthesis of nitrogen doped porous graphitic carbon: Electrochemical determination of paracetamol in presence of ascorbic acid and *p*-aminophenol

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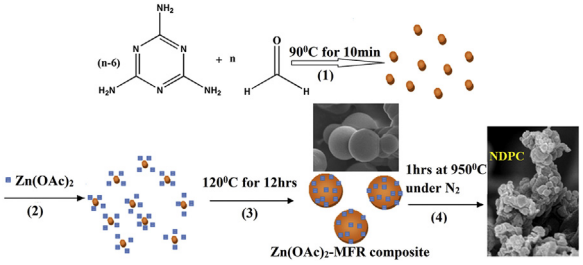
HIGHLIGHTS

- Synthesis of porous nitrogen doped carbon using zinc acetate as hard template from easily available precursors.
- Nitrogen doped carbon shows superior electrocatalytic properties.
- Analysis of paracetamol in biological and pharmaceuticals sample.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphite paste electrode modified with nitrogen doped porous carbon (NDPC) is used for the detections of paracetamol (PCM), ascorbic acid (AA) and *p*-aminophenol (PAP) at relatively low concentration. NDPC is synthesized by direct carbonization of $Zn(OAc)_2$ incorporated melamine-formaldehyde resin microsphere. The NDPC shows small pore diameters centered at 3.14 nm and 8.12 nm and has a pseudo graphitic structure with reasonable porous matrix. The lower limit of detections (S/N = 3) for PCM, AA, and PAP are found to be 30 nM, 720 nM and 10 nM respectively. Under optimized experimental condition, the linear ranges of determination for PCM and AA are 1–400 μM, 10–2700 μM respectively in mixture. Similarly for PCM and PAP mixture, the linear ranges of determination are found to be 1–90 μM. It is also used for the analysis of urine and pharmaceutical products with better sensitivity.

1. Introduction

Paracetamol (PCM) is a well-known antipyretic, non-steroidal and anti-inflammatory drug. It is used mostly for pains associated with backache, headache, cancer, arthritis, postoperative condition and also with viral and bacterial fever [1–3]. Recent studies reveal that it is a preventive for hardening of artery in cardiovascular disease [4]. Recommended doses of PCM do not have any side effect, but overdoses could bring adverse side effects like hepatoxicity and nephrotoxicity [5,6], it also causes liver disorders, skin rashes and inflammation in pancreas [7]. PCM is easily excreted in urine after oral administration due to its rapid absorption and

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distribution. So for monitoring PCM concentration in biological fluid, the analysis of urine sample is convenient. The hydrolytic product of PCM is *p*-aminophenol (PAP) which has adverse side effects on kidneys and physiological growth of the body. The lower limit of body tolerance of PAP is 50 ppm [8]. So monitoring of PAP in the presence of PCM in biological fluid is desirable after administration. Therefore, development of fast, simple and accurate analytical technique for the determinations of PCM and its hydrolyzed product is of great importance. Ascorbic acid (AA) is a natural antioxidant and an important vitamin in living system [9]. AA has an important role in collagen formation and helps in iron uptake through reduction [10]. It is used as an auxiliary medicine for common cold, mental illness, infertility, cancer and AIDS [11]. The metabolic product of AA is oxalic acid, which causes the renal problem. Deficiency of AA leads to anemia, deterioration of collagen, skin hemorrhages, lowering the body resistance from infections [12]. It also causes thyroid deficiency and premature aging [13]. On the other hand, high level of AA causes gastric irritation and diarrhea [14]. Also AA is an interfering biomolecule during PCM analysis in body fluid. Thus, analyses of mixtures of PCM with PAP and PCM with AA are of great importance. Several analytical techniques for above mentioned analysis have been developed using liquid chromatography [15], spectrophotometry [16], chemiluminescence, flow injection methods [17], capillary electrophoresis [18], colorimetry [19], FTIR-Raman spectrometry [20]. But these methods are often expensive and time consuming with low sensitivity and selectivity. As PCM, PAP and AA are electroactive compounds; therefore electrochemical technique for the determination of PCM drew a lot of attention in the last few years due to its simplicity, low cost, high sensitivity and selectivity.

Carbon materials with porous morphology, small pore diameter and large surface area have taken lots of attention for better electrocatalytic properties [21–24]. In this regard, electrode materials made up of carbon nanotube film modified glassy carbon electrode [25–31], graphene modified glassy carbon electrode [32], Nafion/TiO_2-graphene modified electrode [33], C_{60}-modified glassy carbon electrode [34], polyaniline-multi wall carbon nanotube electrode [35], carbon film resistor electrode [36], hematoxiline biosensor [37], polyphenol oxidase modified glassy carbon electrode [38], multiwalled carbon nanotube/pyrolytic graphite electrode [39] and boron doped diamond thin film electrode [40] have been developed.

In this present study, a paste of simple composite of nitrogen doped porous carbon (NDPC) with graphite is used as electrode which shows better sensitivity than all the above mentioned methods. We have synthesized porous nitrogen doped carbon by carbonizing $Zn(OAc)_2$ incorporated melamine formaldehyde resin (ZAIMFR) microsphere. Here $Zn(OAc)_2$ is used as an activator. Comparative study of electrocatalytic properties of nitrogen doped porous carbon-graphite paste (NDPC/GP), bare NDPC, bare graphite paste (GP) electrode against PCM, AA and PAP are investigated. Selective determination of PCM in the presence of AA and PAP is done by using differential pulse voltammetry technique. It is observed that the composite of the NDPC/GP electrode shows better analytical performance amongst all the developed electrodes.

2. Experimental

2.1. Chemicals and reagents

Formaldehyde, Zinc Acetate dihydrate, Ascorbic acid, *p*-aminophenol, Paracetamol, Sodium dihydrogen phosphate, Sodium hydroxide, and Paraffin oil were obtained from Merck, India and Graphite flakes, Melamine were purchased from Sigma Aldrich, USA. All the reagents were analytical graded and used without further purification. All required solutions were prepared using Millipore water (Resistance 18 M Ω).

2.2. Apparatus and measurements

The morphology of synthesized NDPC was determined by JEM2100 high resolution transmission electron microscope (HRTEM) and JEOL JEM6700F field emission scanning electron microscopy (FESEM). The TEM sample was prepared by drying a droplet of suspended NDPC on a carbon coated Cu grid. Nitrogen adsorption-desorption isotherms and Brunauer–Emmett–Teller (BET) surface areas were measured by using Beckmam Coulter SA3100 at 77 K. The sample was degassed at 130 °C for 3 h. Powder X-ray diffraction (PXRD) was carried out with an X-ray diffractometer (XRD, D/MAX-RA, Japan) operated at 40 KV and 40 mA with $Cu_{K\alpha}$ radiation ($\lambda = 0.15406$ nm). Fourier transform infrared (FTIR) spectra (KBr dispersed pellets) in the range of 400–4000 cm^{-1} (model Paragon-500 FTIR of Perkin Elmer spectrometer) and Raman spectroscopy were performed with a micro-Raman system (Renishaw, RM1000-In Via) at 514 nm. The nitrogen content in NDPC was determined using an elemental analyzer (Vario EL III, Germany). All electrochemical measurements were performed by three electrode system using Autolab Potentiostate/Galvanostate101 (Netherlands). An Ag/AgCl electrode was used as a reference electrode and Pt electrode as a counter electrode. All the electrochemical studies were carried out in 0.1 (M) phosphate buffer of pH 6 at temperature 25 ± 2 °C.

2.3. Synthesis of nitrogen doped porous carbon

Formaldehyde (9.8 g, 37%) was added to 200 ml of millipore water in a beaker and heated up to 80 °C and subsequently 2.5 g of melamine was added to it and stirred till to get a clear solution. 1.5 g $Zn(OAc)_2$, $2H_2O$ was added to the above clear solution with continuous stirring and immediately the solution turned turbid, which disappeared with the addition of a few drops of acetic acid. After that, the solution was kept in a hot air oven for 12 h at 120 °C to produce a white powdery mass.

To obtain NDPC, the white mass was then carbonized in horizontal tube furnace at 950 °C for 1hr with a heating rate of 7 °C/min under the continuous flow of N_2 gas. The obtained black powder was collected and complete removal of Zn species was confirmed by Energy dispersive X-ray spectroscopy (EDS) (Fig. 2d).

2.4. Preparation of the NDPC/GP electrode

Graphite flakes and prepared NDPC were mixed in 1:1 (w/w) ratio in a mortar and paraffin oil was added, followed by grinding for making a paste. Finally, the paste was put into a capillary glass tube of 2 mm inner diameter and packed tightly by pressing with a metal rod. Electrical connection was taken by putting a Cu-wire from the backside of the glass tube. Bare graphite and NDPC paste electrodes were prepared in the similar method. Before experimentation, electrode surface was cleaned with 0.3 μm and 0.05 μm Al_2O_3 slurries, rinsed with ethanol and dried under N_2.

3. Results and discussions

3.1. Formation mechanism of NDPC

Scheme 1 is showing a graphical representation of the formation of NDPC, which is synthesized through four major steps. In the 1st