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SYNTHESIS, CHARACTERISATION AND ELECTROANALYTICAL APPLICATIONS OF NITROGEN DOPED ORDERED MESOPOROUS CARBON FOR THE SELECTIVE DETERMINATION OF DOPAMINE, L-CYSTEINE, ASCORBIC ACID AND PARACETAMOL

K.G.Sangeetha[1], R. Vasanthi[2]

P.G & Research Department of Chemistry, D.G. Vaishnav College, Chennai 600 106, Tamil Nadu, India
sangeethabalaji79@gmail.com vasnithraj@gmail.com

Abstract:-

Objectives:

To synthesize CMK-3 Carbon and study its application as modified electrode in three electrode cyclic voltammetry.The modified electrode using CMK-3 Carbon is used for selective determination of Dopamine (DA), L-Cysteine (CY), Ascorbic acid (AA) & Paracetamol(PA).

Findings:

The mesoporous carbon CMK-3 was synthesized using SBA-15 as the hard template and honey as the natural carbon source. The SBA-15 was synthesized using Tetra Ethyl Ortho Silicate (TEOS) as the silica source & Pluronic (P123) as the structure –directing agent. The CMK3 thus obtained was systematically characterized by XRD, BET, SEM and TEM. The low-angle XRD patterns of ordered mesoporous silica (SBA-15) and carbon (CMK-3) reveal that the diffraction pattern of the mesoporous carbon is replicated the parent structure of SBA-15. The TEM and SEM results showed that the hexagonal symmetric pore structures of CMK-3 were highly ordered and the surface area was found to be 587.8 m^2/g. The electrocatalytic behaviors of ordered mesoporous carbon (OMC) modified electrode towards the oxidation of dopamine (DA) and ascorbic acid (AA) L-Cysteine (Cy) and reduction of Paracetamol (Acetaminophen)(PA) were studied by cyclic voltammetry. The OMC modified electrode showed high electrocatalytic activities toward the oxidation of DA and AA, CY and reduction of paracetamol and resolved their voltammetric responses into well-defined peaks. Thus the modified carbon electrode can be used for the selective determination of these types of drug components.

Novelty/Improvement:

For the first time "Honey" was used a source for production of CMK-3 Carbon and utilized for selective determination of DA,CY,AA & PA

Keywords: CMK-3, Modified carbon Electrode, Cyclic Voltammetry, electro catalytic activity.

1. Introduction:

In recent research several carbon-based materials including the carbon fibre,boron doped diamond film, exfoliated graphite etc., have been explored for the electrochemical detection and separation of Dopamine(DA), Ascorbic Acid(AA) ,L-Cysteine(CY) & Paracetamol(PA) [1,2].Presently the Nitrogen- doped carbon as received increasing attention as Oxygen Reducing

Reaction(ORR) catalyst.Nitrogen-doped grapheme [3],carbon spheres[4] ordered mesoporous graphic arrays[5] carbon nano tubes[6] and ordered mesoporous carbon have been reported as the ORR catalyst.In the present investigation,we have developed a mesoporous carbon using Honey as the Carbon source.Natural Honey is a polysaccharide contains a content of 80-85 % Carbohydrates,15-17% Water,0.3% Proteins,0.2% ashes and minor quantities of amino acids and Vitamins that supply supply carbon and nitrogen atoms[7].Our result showed that prepared N-OMC s having nitrogen satisfactory electro catalytic activity.In this report,we present the electrochemical properties of the ordered mesoporous carbons which were prepared by using the Mesoporous Silica materials SBA-15 as the template and Honey as the Carbon Source. Different types of Carbon based electrodes have emerged over the last few years ,significantly widening the scope and improving the sensitivity of electrochemical sensors.Recent studies showed that Omc has attractive

properties such as ion exchange and size selectivity[8],controlled pore distribution and widely accessible active centres [9].These properties have been intelligently combined to selected redox process to design novel sensors & biosensors.Jia & co-workers reported that the catalytic property for the Oxidation of Ascorbic Acid(AA) & Dopamine(DA) can be attributed to the existence of a large amount of edge-plane defect sites in the OMC materials[10].In our present investigation we have utilized the advantages properties of CMK-3 Carbon for application as modified electrodes. The Pt electrode has been modified as CMK-3 mesoporous carbon electrode. The modified OMC electrode was utilized for the simultaneous determination of most essential drugs like Ascorbic acid, Dopamine, Paracetamol & L-cysteine. Although several papers have been published for the simultaneous determination of Ascorbic acid, Dopamine & Uric acid no report has been published for the simultaneous determination of AA,DA,CY & PA in the presence of 0.1 M phosphate buffer solution (pH = 7.5) . The CMK-3 carbon generated from Honey shows excellent sensitivity & selectivity toward the determination of CY & PA in the presence of AA &DA.

2. Experimental

2.1. Chemicals and apparatus

Honey was purchased from local supermarket. Pluronic P123(non-ionic triblock copolymer,(EO20PO70EO20) were obtained from Sigma–Aldrich. Tetra ethyl ortho silicate was obtained from Merck Specialities Private Ltd.. Double distilled water was used to prepare aqueous solutions.Ascorbic Acid (AA),Cysteine (CY) , Paracetamol(PA) & Dopamine(DAwere also purchased. The phosphate buffer solutions (PBS, 0.1M) with various pH values were prepared by mixing stock standard solutions of NaH_2PO_4 and Na_2HPO_4.

Electrochemical measurements were performed on a CH silicone Voltammetric Analyzer model 604E electrochemical workstation (CHI, USA) with conventional three-electrode cell. The ordered mesoporous carbons (OMC) modified Pt electrode, a platinum wire electrode and a saturated calomel electrode (SCE) Ag/AgCl, KCl were used as the working electrode, counter electrode and reference electrode.A digital pH/mV meter model 780 Metrohm was applied for the preparation of the buffer solution. All experiments were performed at an room temperature of 25 ± 2 ºC. Experiments were carried out at room temperature. Transmission electron microscopy (TEM) images,Scanning electron microscope(SEM) Brunauer–Emmett–Teller(BET).were taken.

2.2 SYNTHESIS Of SBA-15 &CMK-3:

The silica templates (SBA-15) were synthesized using PluronicP123 as the surfactant and tetraethyl orthosilicate as the silicasource . The synthesis of pure siliceous SBA-15 materials was accomplished through the method reported by Zhao et al[18]. 4 g P123, 30 ml of double distilled water and 120 ml of HCl (2 mol l−1) were stirred at room temperature. After the complete dissolution of P123, 9 ml of tetraethyl orthosilicate was added to the solution,which was stirred for 20 h at 38◦C. The reaction mixture was then transferred to a Teflon-lined and placed in an oven for 24 h at 100◦C.The product was filtered, dried in a 60◦C oven for 6 h, and calcined at 550◦C for 12 h in air to give the product as a white powder. White precipitate was powdered by using in mortar and pestel.

1 g SBA-15 were added to a solution obtained by dissolving 1.25 g of Honey & 0.14 g of H_2SO_4 in 5 g of H2O, and stirred at room temperature to obtain a homogeneous solution. Then the solution was placed in a oven for 6 h at 100◦C..Subsequently, the oven temperature was raised to 160 ^{0}C for another 6 h.To obtain fully polymerized and carbonized sucrose inside the pores of the silica template, as described above. The composite was treated again at 100◦C for 6h & 160^0 c for 6 h after the addition of 1.6g of honey and 10 g of H2O The template-polymer composites were then pyrolyzed in a nitrogen flow at 900 ^{0}C and kept under these conditions for 6 h to carbonize the polymer. The mesoporous carbons were obtained after dissolution of the silica framework in 5 wt% hydrofluoric acid, (Hydrofluoric acid is harmful to the human and it should be carriedout) by filtration, washed several times with ethanol, and dried.

2.3. Preparation of the ordered mesoporous carbons (OMC) modified electrode:

The Platium electrode (Pt) was polished to a mirror-like surface with alumina slurry followed by rinsing thoroughly with doubly distilled water. The electrodes were successively sonicated in 1:1 nitric acid, acetone and doubly distilled water, and then allowed to dry at room temperature. Twenty microlitre of 0.6 mg/mL mesoporous carbon(CMK-3) 1-methyl-2-pyrrolidone suspension was coated on the surface of pretreated Pt electrode and dried under at room temperature to obtain the CMK-3 modified electrode.

3.Results and Discussion

3.1 Characterisation of CMK-3:

Fig 1 & 2 shows The XRD pattern of the synthesized carbon materials) also confirms that this materials possess a hexagonally ordered mesostructure, as is evident from the presence of at least three XRD lines in the range of 2Θ below 3.0 ^{0} that can be indexed to (100), (110), and (200) reflections of the two-dimensional hexagonal space group p6mm.Consequently, the synthesized carbon material is exactly an inverse replica of SBA-15. and their carbon-coated products. Both of SBA-15and CMK-3 show a sharp XRD peak around 2Θ below 3.0 ^{0}, which corresponds to (1 0 0) planes of the 2D hexagonal lattice. Such a sharp peak was still observed for each carbon-coated sample, indicating that the ordered structure of SBA-15 is preserved after the carbon-coating. The XRD of CMK-3 clearly reflects two distinct peaks that are commensurate with a hexagonal mesostructure, which suggests that the hexagonal mesostructure of the SBA-15 template was preserved after the replication.

Fig 3&4 shows The morphology and microstructure of CMK-3 were investigated by means of SEM and TEM Here, the sample CMK-3. As indicated in Fig.3 the SEM images of CMK-3 reveal the formation of a uniform distribution of nearly short rod-like carbon microstructures. Fig.4 show the TEM images CMK-3 the hexagonal pore arrangement, and clearly display the hexagonal arrays of nitrogen-doped carbon with mesopores existing between the nanorods SBA-15 wall. It can be seen from TEM images that the synthesized carbon materials consist of the ordered

hexagonal array of carbon nanorods. The carbon nanorods are interconnected by spacers, which are constituted by the carbon that filled the channel-interconnecting micropores within the SBA-15.

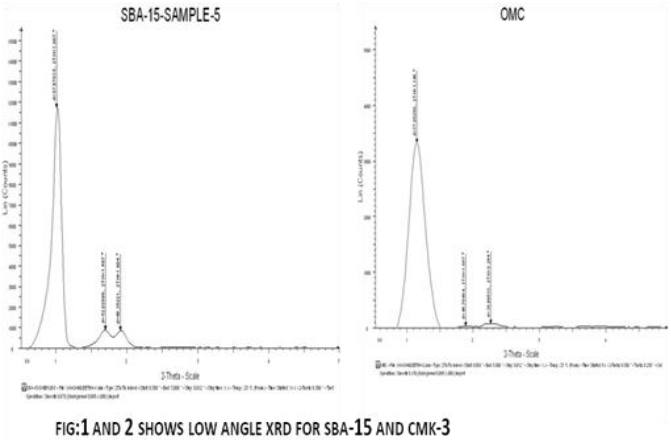


FIG:1 AND 2 SHOWS LOW ANGLE XRD FOR SBA-15 AND CMK-3

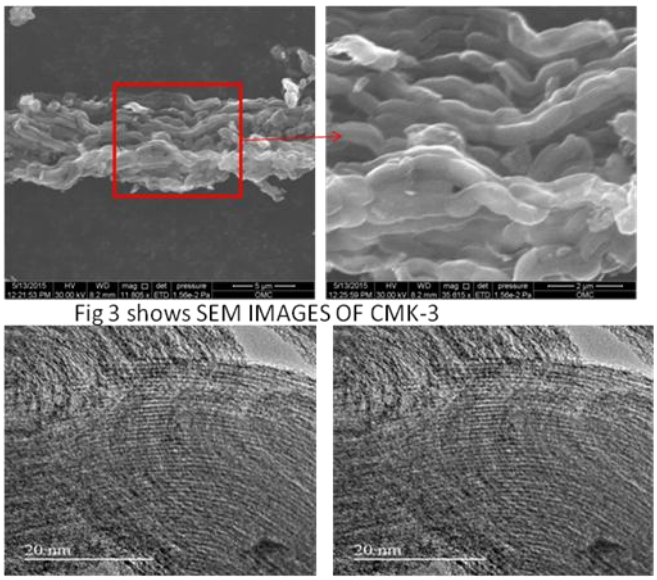


Fig 3 shows SEM IMAGES OF CMK-3

Fig 4 shows TEM IMAGES OF CMK-3

Fig 6 shows The N2-adsorption isotherms of the mesoporous carbon CMK-3 shows The N2-adsorption isotherms of themesoporous carbon exhibits its high specific surface area Pore size distribution of the mesoporous carbon structure was analyzed by the nitrogen adsorption-desorption isotherms in Figure 3A as shown, it exhibits capillary condensation steps on the nitrogen adsorption isotherm and consequently narrow mesopore size distributions. The specific surface area of CMK-3 is calculated to be 578.8375 m^2g^{-1} , with the average pore diameter have quite narrow pore size distribution centered at of 3.91 nm and the specific pore volume of 0.574796 cm^3/g. Fig 5 shows BJH Adsorption dV/dlog(D) Pore Volume.

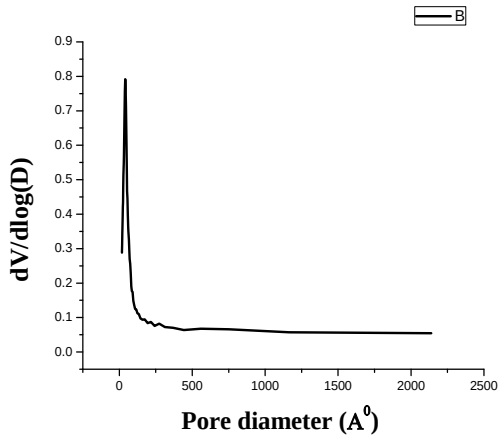


Fig 5

Fig 6

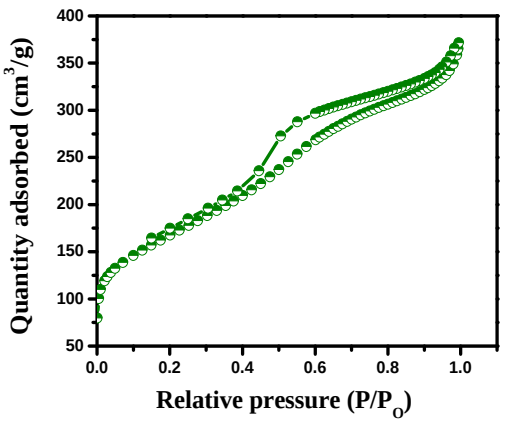


Fig 5 shows BJH Adsorption dV/dlog(D) Pore Volume and

Fig. 6 shows Nitrogen adsorption–desorption isotherms for CMK-3.

Table 1 Structural and textural properties of CMK-3

BET Surface Area(m²/g)	External Surface Area (m²/g)	Micropore Area (m²/g)	Pore Volume(cm³/g)	Micropore volume(cm³/g)	BJH Adsorption Pore volume (cm³/g)	BJH desorption Pore volume (cm³/g)	Pore diameter (Å)	BJH Adsorption Pore diameter (cm³/g)	BJH Adsorption Pore volume (cm³/g)
587.8285	480.9706	106.8579	0.574796	0.048795	0.445133	0.471589	39.1131	44.882	41.646

4.Electrochemical Behaviours of AA,DA,CY &PA:

Electrochemical Characterisation of modified Pt electrode using CMK-3.

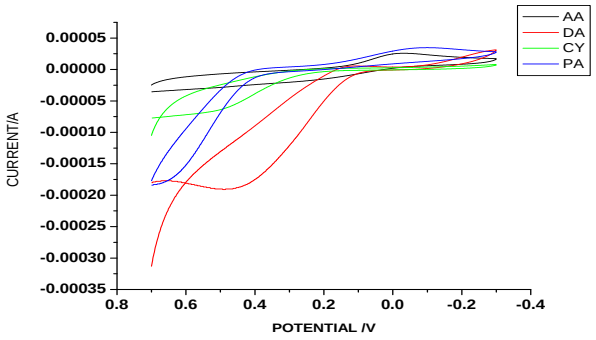


FIG:7A

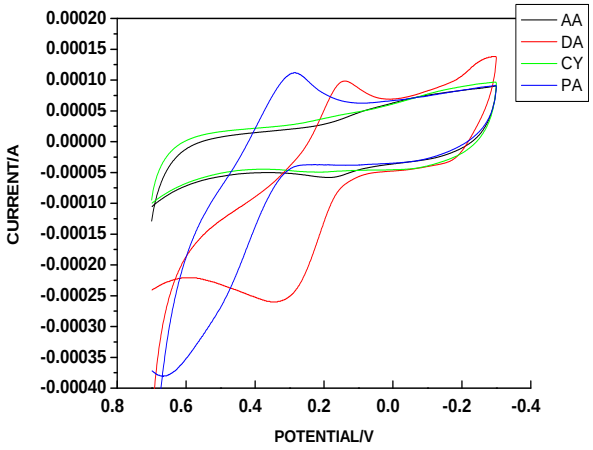
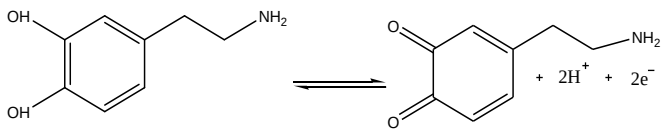


FIG 7B

Fig 7A shows the Voltammetry results bare Pt in 0.1 M PBS (Poly Buffer Solution at pH 7.5 for 5Mm of AA,DA,CY and PA. Fig 7B shows the Voltammetry results of Pt modified into CMK-3 Carbon in 0.1M PBS pH 7.5 for 5Mm of AA,DA,CY and PA.

CMK-3 electrode in Dopamine:

Dopamine (3,4-dihydroxyphenylethylamine) is an important neurotransmitter of the catecholamine group that exists in themammalian central nervous system and is well characterized by its electrochemical activity[11]. The DA level in extracellular fluid is monitored during the neurotransmission processes in patients for diagnose Parkinson's disease.



DOPAMINE DOPAMINE-O-QUINONE

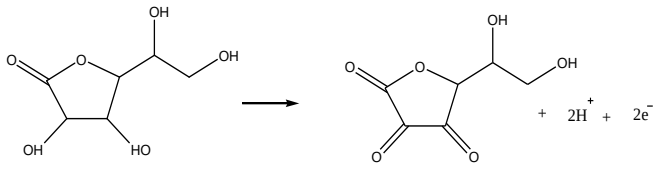
The Dopamine in aCyclic voltammogram should exhibit an anodic peak due to oxidation to dopamine-o-quinone & a cathodic peak due to reduction of to dopamine-o-quinone to dopamine.The present work with bare Pt in 5mM DA with 0.1 M PBS of PBS at pH 7.5 showed oxidation peak at 0.448V with 10^{-4} A peak current and a weak reduction peak. Irreversible behaviour of bare Pt was observed. CMK-3 electrode in 5mM DA with PBS at pH 7.5 showed a reversible or equilibrium reaction of DA.An anodic peak at 0.322 V with

10^{-4} peak current and cathodic peak at 0.139V with 10^{-5} A peak current.CMK-3 electrode was able capture the reversible behaviour or the equilibrium reaction of DA.

CMK-3 in Ascorbic acid:

Ascorbic acid is a water – soluble reducing agent. Ascorbate ($ASCH^-$) act as donor antioxidant can undergo two consective,one electron oxidations resulting in the formation of ascorbate radical (Asc•−) and dehydroascorbic

acid (DHA)[12]. Ascorbate ions which have neurological applications & anti-cancer property in mammals.



Ascorbic acid Ascorbate

In Our present investigation 5mM AA in 0.1 PBS at pH 7.5 with bare Pt as working electrode does not show any genuine oxidation peak.Whereas when bare Pt is replaced by modified CMK-3electrode it exhibited a peak at 0.188V with peak current of 10^{-5} A (ampere).Therefore CMK-3 electrode can be used as a definitely sensor for determining the presence of AA.Since AA plays a vital role in bioelectrochemistry, neurochemistry and clinical diagnostic applications

CMK-3 electrode in L-Cysteine :

L-Cysteine (CySH) is an important amino acid owing to its crucial roles in biological systems. , It is a prospective radiation protector and cancer indicator.[13-16]Moreover, the couple L-cystine/L-cysteine is generally used as a model for the role of the disulfide bond and thiol group in proteins in a variety of biological media.1 Therefore, it is very important to investigate the electrochemical behavior and sensitive detection of CySH [17].

The electrochemical oxidation of CySH on solid electrode may proceed by the following mechanism

$$CySH \leftrightarrow CyS^- + H^+$$

$$CyS^- \rightarrow CyS^*_{ads} + e^-$$

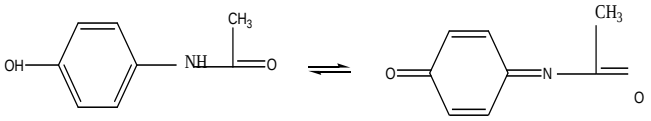
$$2\ CyS^*_{ads} \rightarrow CySSCy$$

In the present study in 5mM CySH with 0.1 PBS at pH 7.5 shows a weak positive anodic peak at 0.518 V with 10^{-5} A peak current.CMK-3 in 5Mm CySH with 0.1 PBS at pH 7.5 shows a broad rectangular pattern in cyclic voltammogram.This indicates the high current generation .An anodic peak at 0.153 with 10^{-5} A indicates the oxidation of CySH to CySSCy.

An anodic peak at 0.153 with 10^{-5} A indicates the oxidation of CySH to CySSCy.

CMK-3 electrode in Paracetamol :

Paracetamol (Acetaminophen or , N-acetyl-p-aminophenol) is a long-established substance being one of the most extensively employed drugs in the world. It is an antipyretic and analgesic drug commonly used against mild to moderate pain or for reduction of fevers.



PARACETAMOL N-acetyl benzoquinone imine

In the present study the Paracetamol(PA) showed irreversible behaviour was studied by bare Pt electrode .The Cyclic voltammogram using bare Pt electrode in 5m M PA with peak current 10^{-5} A. The similar behaviour was also observed while using CMK-3 Carbon electrode.The peak potential at 0.293 V with peak current 10^{-4} .The peak current was enhanced on using CMK-3 electrode.The oxidation behaviour was not observed because of the absence of inert atmosphere .In the presence of Argon gas,then the equilibrium established between N-acetyl-p-benzoquinone imine & Paracetamol would have been definitely observed.

Simultaneous determination of DA,AA,CY and PA at the CMK-3 electrode by Cyclic voltammetry (CV):

To verify the feasibility of the simultaneous determination of DA, AA,CY and PA at CMK-3 ,CV was carried out in their mixture DA,CY and AA coexist in the extracellular fluid of the central nervous system and serum.Overdose ingestions of PA lead to accumulation of toxic metabolites, which may cause severe and sometimes fatal hepatotoxicity and nephrotoxicity, which in some cases associate with renal failure. The ability to selectively determine these species has been a major goal of electroanalysis research. Therefore,the electrochemical behaviors of DA,AA,CY and PA in a mixture solution were studied.

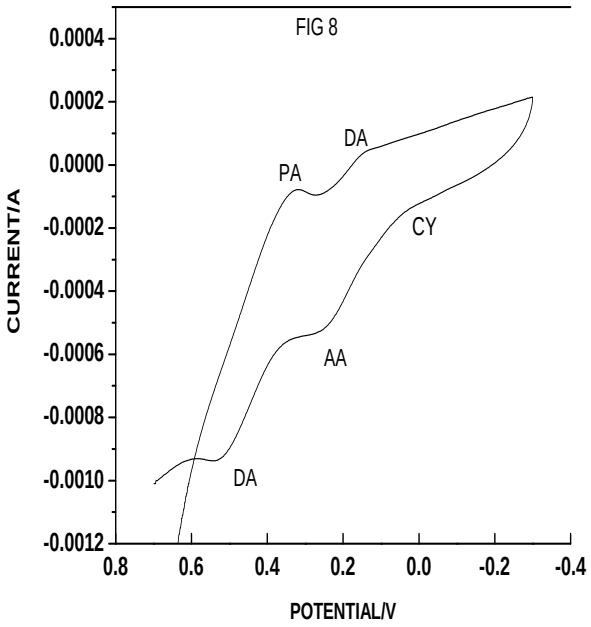


Fig 8 shows the cyclic voltammogram of simultaneous determination of DA, AA,CY and PA at CMK-3 was carried out in their mixture in 0.1 PBS at pH 7.5.Two anodic peak at 0.526 V& 0.250 V shows the presence of DA & AA oxidation states.Two cathodic peaks at 0.326V & 0.139 V shows the presence of PA and DA reduction states.A very mild anodic peak at 0.153 V may be due to CySH oxidation DA,AA,PA and PA were been simultaneously captured electrochemically by CMK-3.The higher concentration of Cysteine would have exhibited a prominent Oxidation peak.

The CMK-3 carbon generated from Honey shows excellent sensitivity & selectivity toward the determination of CY & PA in the presence of AA &DA. Honey as a carbon source for CMK-3 to do the electrochemical studies of DA,AA,CY and PA. Nitrogen- doped carbon as received increasing attention as Oxygen Reducing Reaction(ORR) catalyst The results showed here the electrocatalytic behaviors of the CMK-3 modified electrode towards the oxidation of DA ,AA,CY and reduction of AC were investigated.The ordered mesoporous carbons showed a faster electron transfer rate compared to GC electrode. The CMK-3 modified electrode exhibited high electrocatalytic activities toward the oxidation of DA ,AA,CY and reduction of PA ,and displayed good voltammetric peak separation between DA , AA,CY and PA. The strong electrocatalytic ability of CMK-3 resolves the overlapping peaks, lowers the overpotential, and greatly enhances the current response for the oxidation of DA, AA, CY and reduction of PA.Thus, CMK-3 carbon electrode is highly sensitive and suitable for potential electrochemicalsensor applications

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