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Research Article

Electrochemical Characterization of Sky Honey Mediated by Glassy Carbon Electrode Modified with Carbon Nanotube

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Abstract

Sky honey (SH), a kind of sweet was studied to identify its uses in human lives and its applications in different areas. Electrochemical analysis by cyclic voltammetry was used to characterize SH in aqueous solution. Glassy carbon electrode (GCE) was modified with carbon nanotube (CNT), i.e. CNT/GCE by mechanical attachment method via cyclic voltammetric technique to study the oxidation-reduction current peaks of SH at different electrolytes, concentrations, scan rates, pH and temperatures. Moreover, the study included the reliability and stability of CNT on the GCE surface.

Keywords: CNT/GCE; Cyclic voltammetry; Sky honey; Electrolytes; Human blood

Introduction

Sky honey (SH) is a drizzle that descends from the sky on trees or rocks, becomes sweet and turns into honey, and dries like a gum. The electrochemistry of glass carbon electrode (GCE) modified with carbon nanotube (CNT) in different electrolytes using cyclic voltammetry (CV) has been studied, and has also been studied in blood medium [1-5]. A sensor for the qualitative analysis of honey based on carbon paste electrode modified with nickel oxide nanoparticles has been reported. The resulting modified carbon paste electrode combined the electrochemical properties of carbon paste electrode with the advantages of metal oxide nanoparticles. The modified electrode has been used to study the floral type of various honey samples using CV technique. The new electrode revealed interesting electro-catalytic behavior towards floral characterization of honey [6]. Honey quality evaluation is a complex task and is carried out by traditional technique using CV method by platinum working electrode. The use of principal component analysis (PCA) has been proved useful in characterizing honey samples from different botanical origins [7]. Fourteen commonly available types of cane and palm sugar were analyzed for antioxidant activity using CV. Five of the sugars dissolved in phosphate buffer, showed anodic current peaks which were indicative of antioxidant activity. The rank order of these sugars was: gula anau > gula merah > China rock honey sugar > soft brown sugar > raw sugar. It was concluded that from a nutritional point of view, using gula anau as a sweetener or ingredient in foods or drinks had an added benefit owing to its antioxidant content [8]. Two different approaches, spectroscopic and electrochemical, were applied for rough determination of antioxidative potential of honey samples. Cyclic voltammograms on a GCE in KCl supporting electrolyte were used to check electrode sensitivity to the presence of honey. CVappeared to be a highly attractive alternative method for rapid estimation of antioxidative potential of honeys [9].

In this study, a new material of sky honey was characterized by CV technique at GCE modified with carbon nanotube (CNT), i.e. CNT/GCE, to determine the electrochemical behavior in different electrolytes, temperatures, scan rates, concentrations and pH.

Experimental

Extraction of sky honey and chemical reagents

SH was extracted from the collected powder of raw materials in aqueous solution by stirring with heat after filtration of the solution from impurity; a deep yellowish solution was used in the experimental as a stock solution. All experiments were carried out at room temperature of the laboratory (25 °C).

Other chemicals and solvents were of annular grade and used as received from the manufacturer. Deionized water was used for the preparation of aqueous solutions. All solutions were de-aerated with oxygen by free nitrogen gas for 10-15 min prior to making the measurement.

Instrumentation

The EZstat series (potentiostat/glvanostat) were provided from NuVant Systems Inc. Pioneering Electrochemical Technologies, USA. Electrochemical workstations of bioanalytical system with potentiostat driven by electroanalytical measuring soft wares were connected to personal computer to perform cyclic voltammogram. Ag/AgCl (3M NaCl) and platinum wire (1 mm diameter) was used as a reference and counter electrode respectively.

Preparing the modification of GCE with CNT (CNT/GCE)

The mechanical attachment technical method to prepare the CNT/GCE working electrode was employed to prepare nano-sensor [10, 11]. The method of the modification of GCE included abrasive application of multiwall carbon nanotubes (MWCNT) on the clean surface of GCE, where an array of MWCNT was formed as modified working electrode (MWCNT/GCE) and replaced in 10 mL of electrolyte in the cyclic voltammetric cell. Then, all electrodes (working electrode, reference electrode and counter electrode) with the potentiostat were connected.

Results and Discussion

Sky honey was characterized by CV technique at CNT/GCE in different electrolytes, temperatures, pH, concentrations and scan rates.

Effect of different supporting electrolytes

The effect of different supporting electrolytes of KCl, normal saline (NS) (0.9% NaCl), K_2HPO_4 and KH_2PO_5 was studied with regarding to the oxidation and reduction current peaks of sky honey using scan rate 100 mV/sec versus Ag/AgCl as reference electrode. Table 1 shows the redox current peak of sky honey at CNT/GCE as modified working electrode in different electrolytes. The results revealed that the better electrolyte was KCl. The values of oxidation and redaction current peaks of sky honey achieved the same sequence on GCE in different electrolytes as shown in Fig. 1. KCl solution as a supporting electrolyte enhanced the redox current peaks of sky honey with the presence of CNT on GCE surface. The enhancement of redox current peaks was in the following orders:

For $I_{pc\ CNT/GCE} / I_{pc\ GCE}$:

KCl > NS > KH_2PO_5 > K_2HPO_4, and

For $I_{pa\ CNT/GCE} / I_{pa\ GCE}$:

KCl > NS > KH_2PO_5 > K_2HPO_4

It can be seen from Table 1 that the value of I_{pa}/I_{pc} ratio of oxidation-reduction current peaks was nearly to 1 for sky honey in different supporting electrolytes, which indicated that the redox process was reversible [12]. And the separation potential value of oxidation-reduction peak of SH was equal to 100 mV, as shown in Table 1, which indicated that the reaction of SH in KCl electrolyte was a homogenous transfer of electron [13].

Effect of different pH

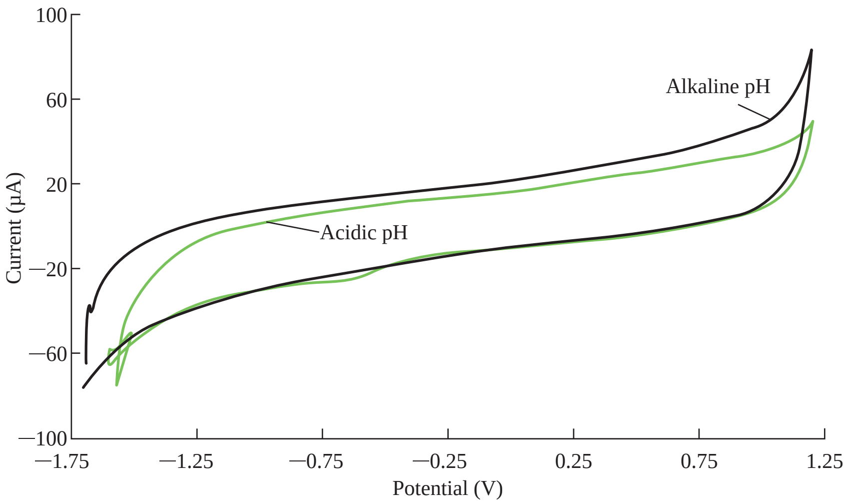

Fig. 1 Cyclic voltammogram of sky honey at acidic and alkaline pH in 0.1 M KCl on CNT/GCE versus Ag/AgCl as reference electrode.

Table 1 Potential and enhancement of redox current peaks of sky honey in different electrolytes at glass carbon electrode (GCE) and glassy carbon electrode modified with carbon nanotube (CNT/GCE)

Electrolyte	CNT/GCE						GCE			
	E_{pa}	I_{pa}	E_{pc}	I_{pc}	$\Delta E_{pa\text{-}c}$	I_{pa}/I_{pc}	E_{pa}	I_{pa}	E_{pc}	I_{pc}
K_2HPO_4	802.9	25.38	618.4	15.6	184.5	1.626923	804	14.53	665.6	12.85
KH_2PO_4	661.3	29.55	685	16.56	23.7	1.78442	661.3	15.02	684.5	12.86
NS	731.9	29.74	613.2	18.22	118.7	1.632272	495.8	19.39	614.2	17.18
KCl	613.9	34.97	612.9	20.23	100	1.728621	496	21.24	613.2	18.45

The effect of both acidic and alkaline pH in 0.1 M KCl for sky honey was studied using modified GCE with CNT (CNT/GCE) as working electrode and Ag/AgCl as reference electrode. The cyclic voltammogram of SH in 0.1 M KCl at different pH is illustrated in Fig. 1. It was observed that the oxidation current peak of sky honey in acidic media (3-7) was gradually linearly decreasing against the increasing of acidity, as shown in Table 2, while in alkaline pH (7-10), the oxidant peak was enhanced to high current. The cathodic current peak of SH was still constant at different pH, as shown in Fig. 2. Table 2 shows that the value of current ratio I_{pa}/I_{Pc} of the sky honey at pH = 4.8 was equal to 1.2 (nearly to 1), meaning that the redox current peak was reversible process at these pH [14].

The other evidence for the reversibility of the redox reaction of sky honey was that the potential peak separation value also equaled nearly to 100 mV, as show in Table 2 [15].

Effect of varying scan rates

The cyclic voltammogram of sky honey in 0.1 M KCl was studied at different scan rates, which

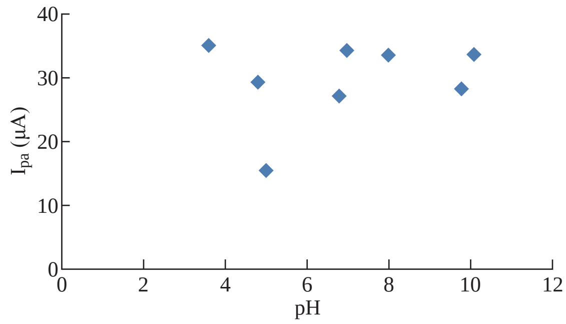

Fig. 2 Effect of different pH (3-10) on the oxidative current peak of sky honey in 0.1 M KCl at CNT/GCE.

expressed that the increasing scan rate followed the increase of redox current peaks, as shown in Fig. 3.

However, the anodic current peak shifted towards to higher potential and the cathodic current peak shifted to the lower potential (Fig. 3). In a slow voltage scan rate, the diffusion layer grew much further from the electrode in comparison to a fast scan rate as a result; the flux to the electrode surface was much smaller at slow scan rates than at faster rates. As the current was proportional to the flux towards the electrode, the current intensity became lower at slow scan rates and

Table 2 Effect of different pH on potential separation and redox current ratio

pH	I_{pa}	E_{pa}	E_{pc}	I_{pc}	E_{pa}-E_{pc}	I_{pa}/I_{pc}
3.6	34.97	613.9	612.9	20.23	1.0	1.7
4.8	29.23	613.8	685.4	24.71	71.6	1.2
5.0	15.37	353.3	685.1	21.37	331.8	0.7
6.8	27.09	709.8	661.5	20.99	48.3	1.3
7.0	34.17	803.6	589.1	25.48	214.5	1.3
8.0	33.44	709.7	541.6	23.70	168.1	1.4
9.8	28.21	613.8	685.1	22.38	71.3	1.3
10.1	33.59	615.4	684.6	23.00	69.2	1.5

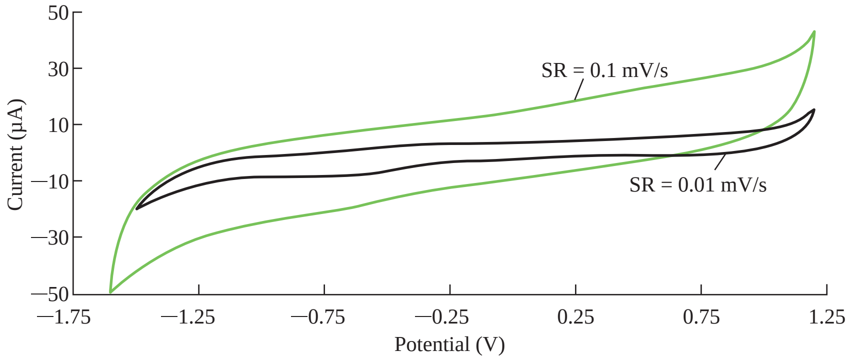

Fig. 3 Cyclic voltammogram of sky honey at different scan rates in 0.1 M KCl on CNT/GCE versus Ag/AgCl as reference electrode.

higher at high scan rates [16].

Effect of varying temperatures

The effect of different temperatures of 9 and 50 °C on the oxidation-reduction process of sky honey in 0.1 M KCl was studied. It was found the oxidation current peak increased gradually at the increasing of temperature (Fig. 4), while the reduction current peak increased against the increasing of temperature. Fig. 5 and 6 are the plot of log I_{pc} (reduction current) and I_{pa} (oxidation current) respectively of sky honey versus reciprocal of temperature, which was found to be fairly linear in agreement with thermodynamic expectation of Arrhenius Equations (1) and (2) [17]:

$$\sigma = \sigma_o \text{ Exp } (-E_a/RT), \quad (1)$$

and

$$D = D_o \text{ Exp } (-E_a/RT), \quad (2)$$

where σ and D are conductivity and diffusibility; σ_o and D_o are standard conductivity and initial diffusibility.

The activation energy (E_a) was calculated from the slope of both cathodic and anodic current peaks of sky honey to find E_a(reduction) = 8.78 kJ/mol.K and E_a(oxidation) = 5.33 kJ/mol.K. Hence, the two activation energy values were convergent because the oxidation and reduction processes of sky honey at different temperatures were reversible reaction with minimum energy.

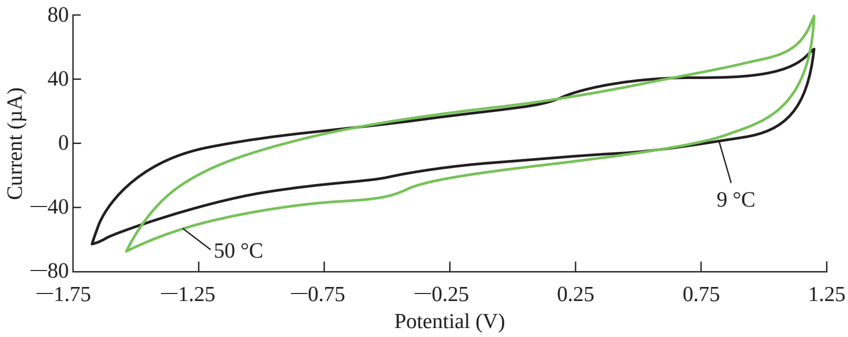

Fig. 4 Cyclic voltammogram of sky honey at 9 and 50 °C in 0.1 M KCl at CNT/GCE as working electrode and Ag/AgCl as reference electrode.

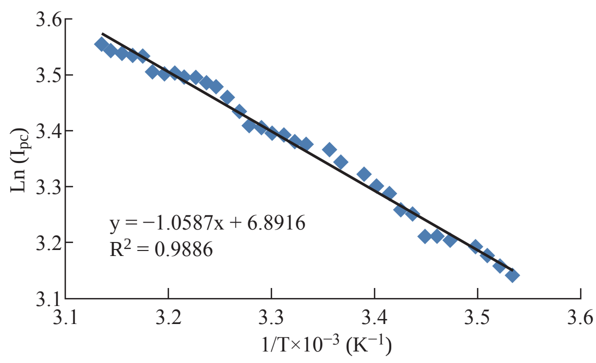

Fig. 5 Effect of different temperatures (9-50 °C) on reduction current peak of sky honey in 0.1 M KCl at CNT/GCE.

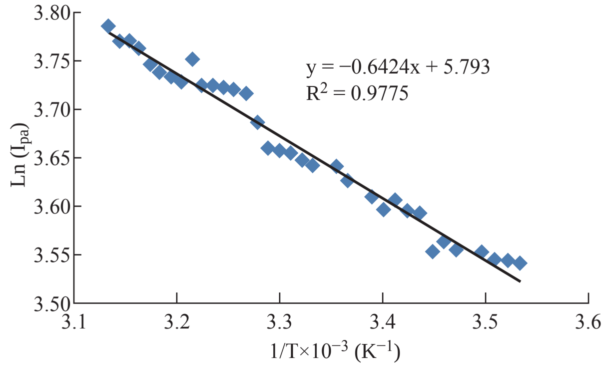

Fig. 6 Effect of different temperatures (9-50 °C) on the oxidative current peak of sky honey in 0.1 M KCl at CNT/GCE.

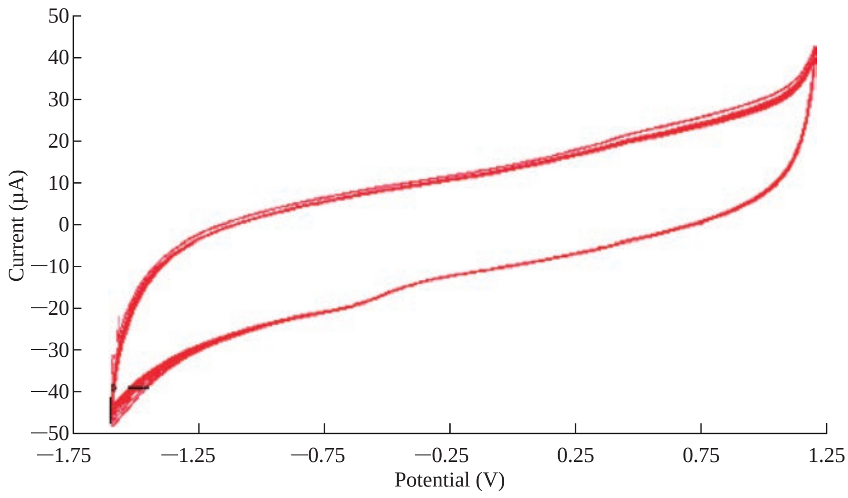

Fig. 7 Cyclic voltammogram of sky honey at ten times of cyclic in 0.1 M KCl on CNT/GCE as working electrode and Ag/AgCl as reference electrode.

Reliability and stability of modified electrode

The potential cycling of the oxidation-reduction current was carried out during CV for the modified working electrode CNT/GCE in sky honey in KCl solution at scan rate of 100 mV/sec. The reliability of current of the anodic current peak (I_{pa}) at the relative standard deviation (RSD) was ±1.95%. Fig. 7 shows the cyclic voltammogram of redox current peaks of sky hone in KCl at ten times of cyclic, which revealed a good stability of CV of the modified GCE by overlapping of the voltammogram lines.

Conclusions

Sky honey (SH), as a new material was studied by electrochemical analysis method using cyclic voltammetric technique with nano-sensor CNT/GCE to determine the electrochemical properties of SH in aqueous solution. The modified electrode (nano sensor) succeeded in enhancing the redox current peaks of SH in different electrolytes, and the best electrolyte was found to be 0.1 M KCl. SH in potassium chloride solution at the modified electrode had good results because of the high quality of reliability and stability to enhance the cathodic peak of SH at different concentrations, scan rates, temperatures and pH.

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Conflict of Interests

The authors declare that no competing interest exists.

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