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Hydrothermal Synthesis of Carbon Coated $NiCo_2O_4$ Nano flower for the Electrochemical Oxidation of Sulfite in Real Sample

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A facile synthesis of carbon-coated nanoflowers C@$NiCo_2O_4$ by using the simple hydrothermal method and nitrogen-rich melamine as a carbon source for electrochemical detection of sulfite. As synthesized materials were analyzed by using the physiochemical methods such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and EDAX mapping conforms the crystal structural, the presence of chemical species, functional groups, flower like morphology and quantity of specific elements of C@$NiCo_2O_4$ respectively. Among the all the prepared sample C@$NiCo_2O_4$-3 are reveals greater electrocatalytic activity by earlier oxidation of sulfite at 0.42 V in cyclic voltammetry studies. Amperometry depicts that the good sensitivity (3.57 µA $mM^{-1}cm^{-2}$), low limit of detection (0.05 µM) and linear range (0.3 to 724 µM) of C@$NiCo_2O_4$-3 due to boosted electrical conductivity by synergetic effect (between coated carbon and $NiCo_2O_4$) and enlargement of surface area. Six time repeatability of single modified GCE of pristine and C@$NiCo_2O_4$-3 CV curve shows oxidation peak current with RSD of 43% and 4% respectively, stable operation of C@$NiCo_2O_4$-3 is owing to chemical inertness of carbon. Real-time detection of sulfite in red wine and tape water guarantee the commercialization of electrochemical sulfite sensor.

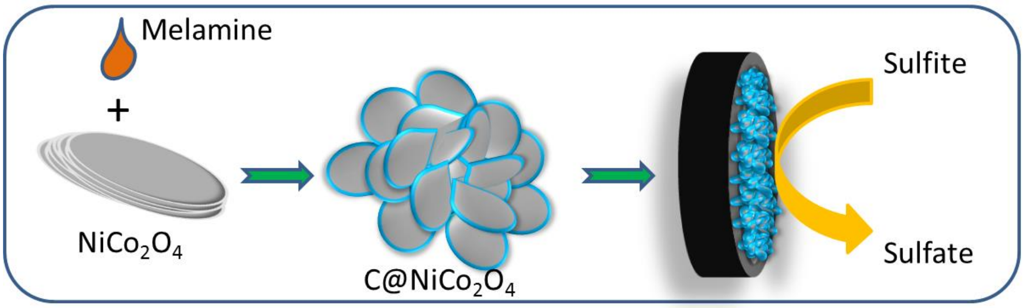
Keywords: Nickel cobaltite, sulfite, electrochemical oxidation, carbon coating $NiCo_2O_4$.

1. INTRODUCTION

Currently, the electrochemical activity of Nano size Binary Transition Metal Oxide (N-BTMO) attracts the attention of many researchers, because of its higher electrochemical activity in electrochemical device namely battery, supercapacitor, fuel cell, HER, ORR, electrocatalyst and the electrochemical sensor. Everything owing good electrochemical activity with much more oxidation states, high surface area, excellent electrical conductivity, simple preparation method, low cost and eco-friendly of N-BTMO [1-7]. Recently Ni, Co, Mn, Sn, Al, Li, Fe, Cu, Zn, based binary or ternary N-BTMO has been used as an electroactive material for the above mentioned applications. Among them, $NiCo_2O_4$ (nickel cobaltite) is extensively analyzed in so many research field. When compared to other N-BTMO it has more advantage many oxidation states, a spinel structure, simple method of preparation, low cost, abundant resources and eco-friendliness [3,8,9]. $NiCo_2O_4$ is a spinal crystal structure binary metal oxide in that Ni occupied the tetrahedral site and Co occupy octahedral site through this benefit it exhibits excellent electrochemical performance with high electrical conductivity through Ni and Co ions better than mono-phase NiO_2, CoO_2 [10]. In other hand morphology of $NiCo_2O_4$ poses crucial role in electrochemical performance by enlarging accessible surface area and easy electron transporting structure. Different kind of approaches was carried out to warp the morphology of $NiCo_2O_4$ including nano needle arrays, tupes, flakes, wires and hexsapods [11], in that way *Mylamparambil et a*l has prepared sheaf like nano porous $NiCo_2O_4$ for electrochemical detection of eugenol [12]. *Huang et al* has reported nano hollow spheres $NiCo_2O_4$ by route template for non-enzymatic glucose sensor [13]. For supercapacitor application Xiang et al prepared dumpple like nano structured by simple hydrothermal method [11]. *Shen et al* has grown mesoporus $NiCo_2O_4$ nano wires on carbon textile for energy storage application [14]. *Veeramani et al* prepared $NiCo_2O_4$ with different fine morphology for energy storing application [15]. The main issue of $NiCo_2O_4$ like electrode material has big problem during electrochemical performance it gets degrade or aggregated into big particle from that it is suffer from decreasing of surface area, increasing of resistance, fading in its performance, rate capability, stability, repeatability and lose its integrity after few cycles because of structural changes and dispersion in electrolyte medium [16,17]. Thus various methods have been followed to save N-BTMO based electroactive material from above-mentioned drawbacks. In order to retain and enhance the electrochemical performance of metal oxide, the carbon-coating is one of the superior techniques because it is a very simple process and also carbon offer more advantage over electrochemical performance chemically inert, large surface area, structure stability, low cost and eco-friendly [18]. Without damaging the crystal structure of the pristine material is difficult in that way different kind of methods and materials has been used to enhance the electrical conductivity, structural stability of electrode material [18-21]**.** Still, now Carbon coating surface modification methodology has been used to prevent the electroactive material of supercapacitor and battery from capacitance fading, additional layer forming, dispersing of material in electrolyte and aggregation. *Veddiyappan et al* have utilized EDOT as a carbon source to coat carbon on $NiCo_2O_4$ for supercapacitor application [7], *Ramkumar et al* have prepared the carbon-coated LiCoMnO by using glucose as carbon source for Li-ion hybrid capacitor [22]. And also our research group recently reported nano size $NiCo_2O_4$ with various morphology by varying concentration of dopamine as carbon source [15]. From the literature hydrothermal synthesis gives easy and efficient results for carbon coating [23].

Sulfite has been majorly used to prevent oxidation, microbial reaction and preserves vitamin C in processed foods and beverages including wine, dried fruit, boiler industries [24, 25]. Foods and beverages should contain allowed the amount of sulfite and also that must be labeled in products due to its toxicity [26]. Natural abundance of sulfite in lake, river and groundwater, it induces the reduction in the concentration of oxygen then it will severely affect the aquatic life [27]. However, the FAO/WHO joint experts committee has indicated when consuming the more amount of sulfite than allowed amount (0.7g/kg of body weight) lead to asthma and some allergic reactions [28, 29]. Thus we have to find out an efficient way to detect sulfite in all forms, Still now so many methods have been used to detect the sulfite as well as chromatography, fluorescence method, colorimetric, chemiluminescence and spectrophotometry but all methods have many problems during sulfite detection such as low sensitivity and selectivity, long time operation, sample pretreatment with high cost when compare to the electrochemical method. Due to direct current detection of sulfite oxidation by the electrochemical method has advantages over than other methods being high sensitivity, selective with low cost and simple operation [30-34].

Here we have reported nitrogen-rich melamine as a carbon source to prepare nanoflower like Spinel carbon-coated $NiCo_2O_4$ (C@$NiCo_2O_4$) for electrochemical detection of sulfite. Prepared C@$NiCo_2O_4$ has displayed good electrocatalytic activity than pristine $NiCo_2O_4$. Carbon coating is giving additional electrical conductivity and enlargement of the accessible surface area to earlier oxidation of sulfite at 0.42 V with comparable sensitivity, low range of detection (LOD) and broad linear range of detection. Best of our knowledge there is no report on C@ $NiCo_2O_4$ for electrochemical detection of sulfite.



Scheme 1 As synthesis of NiCo2O4 with and without carbon coating for the electrochemical oxidation of sulfite.

2. EXPERIMENTAL SECTION

2.1. Materials

Nickel (II) chloride hexahydrate ($NiCl_2.6H_2O$) was purchased from Wako pure chemical industries, LTD. Cobalt (II) nitrate hexahydrate ($Co(NO)_3.6H_2O$) and potassium chloride (KCl) were purchased form Sigma Aldrich. All the chemicals were used as per obtained conditions without carrying the purification for all the experiments.

2.2. Synthesis of carbon coated $NiCo_2O_4$ Nano flower

The carbon coated $NiCo_2O_4$ nano-flower was synthesized by using the hydrothermal method. Briefly, the starting precursors of 3 mM Nickel and 5 mM cobalt was dispersed in 30 ml DD water and ethanol in the 50 ml beaker and ultra-sonicated for 15 minutes. At the end of sonication, the solution was turned into brown color. it After that, the brown solution was kept in magnetic stir and the ammonia solution (0.1 M) was added into the solution as dropwise method to adjust the pH 10 and the resultant solution was light blue in color .The different concentrations of melamine (0.5 M, 1 M, and 1.5 M) were then added to the above solution at continuous stirring for 1h and named as C@$NiCo_2O_4$-2 C@$NiCo_2O_4$-3 and C@$NiCo_2O_4$-4. Then the final resultant solution was transferred into the 50 capacitive Teflon-lined stainless steel autoclave and the treated at 180 ºC for 12 hrs. The light green precipitate was washed with DD water and ethanol for several times and then dried at 60 ºC for overnight. As the final step, the black powder was treated at 350 ºC for 3 hours. The same procedure was adopted for preparing without carbon coated $NiCo_2O_4$ for the effective comparison.

2.3 Characterization methods

The sample morphology was recorded by using a field-emission scanning electron microscope (FESEM-JSM-6500F, JEOL). Energy dispersive X-ray (EDX) spectrum was recorded by using HORIBA EMAX X-ACT equipped with Hitachi S-3000 H scanning electron microscope. Fourier transform infrared spectroscopy (FTIR) measurements were carried out by using JASCO FT/IR-6600. Electrochemical impedance spectroscopy was performed by using IM6ex ZAHNER impedance measurement unit. The cyclic voltammetry, amperometric (i-t) studies were performed by using electrochemical analyzers (CHI 627).

2.4 Preparation of electrode

The as-synthesized composite material (6 mg/ml) was dispersed in the ethanol and ultra-sonicated for 1 hrs. The glassy carbon electrode (GCE) was precleared with (0.05 µM) alumina powder, washed with DD water and ethanol and the dried in air oven. The well precleared GCE surface was drop casted with 6 µL of the prepared solution and dried in air oven. Finally, the modified electrode was washed with DD water to remove the unbound materials, which the performer as a working electrode. All the experiments were prepared in the same process in modified electrode.

3. RESULTS AND DISCUSSION

The pristine $NiCo_2O_4$ sample shows nano-flower like morphology under the Scanning electron microscope. The nano bundle like morphology which nanosheets are unexposed to electrochemical reactions in nanobundle are also observed as shown in Fig 1(a, b). This may be lead to poor electrochemical performance. The addition of melamine for the purpose of introducing carbon on the surface of $NiCo_2O_4$ interestingly aligned the nanobundles into nanoflower in which nanosheets are open to the electrochemical process. Moreover, there was the distinct formation of nanoflower while increasing melamine amount for each amount of carbon source as shown in Fig 1(d, f)). Contradictorily, the nanoflower morphology was started to change for the higher concentration of melamine. Fig 1(c-h) shows the zoomed SEM image of non-uniform nanosheets this may be maximum amount melamine leads to this shape. The orientation of 30 nm thickness $NiCo_2O_4$ nano sheet in all direction leads to carbon-coated $NiCo_2O_4$ with high the surface exposing surface to electrochemical performance as compared to pristine $NiCo_2O_4$.

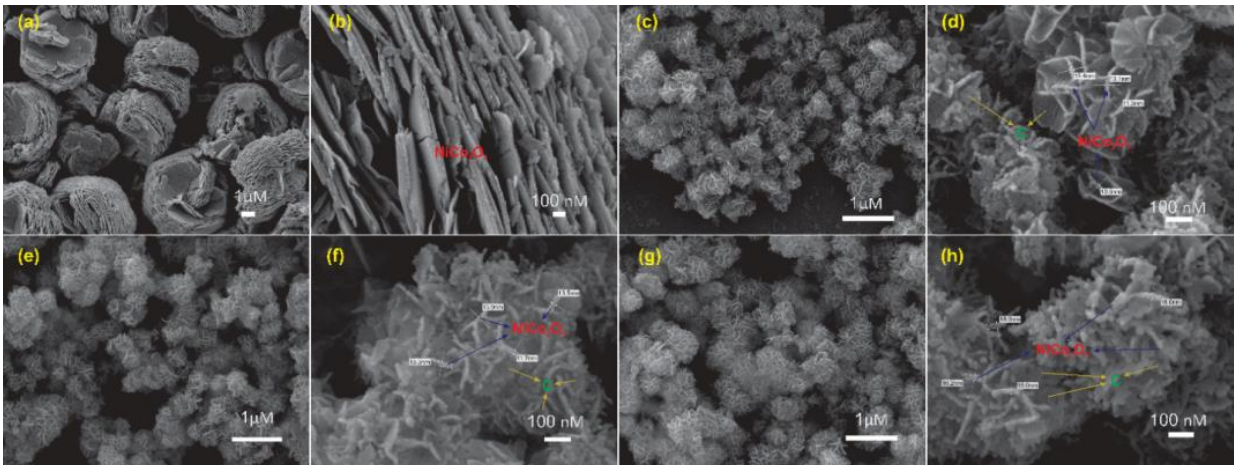


Figure 1. FE-SEM images (a, c, e, g) low and (b, d, f, h) high magnification of of $NiCo_2O_4$ and $C@NiCo_2O_4$ samples.

The EDX spectrum also strongly confirms the presence of element percentage in the prepared sample to the percentage of how much amount of elements contributed to form a compound. The resulted spectrum is showed in fig 2 that assures the formation of carbon and $NiCo_2O_4$. Inside the all Fig 2 table shows how much amount carbon present in $NiCo_2O_4$. The weight percentage of carbon increase with the increment of melamine amount it reveals the carbon coating strongly adhered with $NiCo_2O_4$.

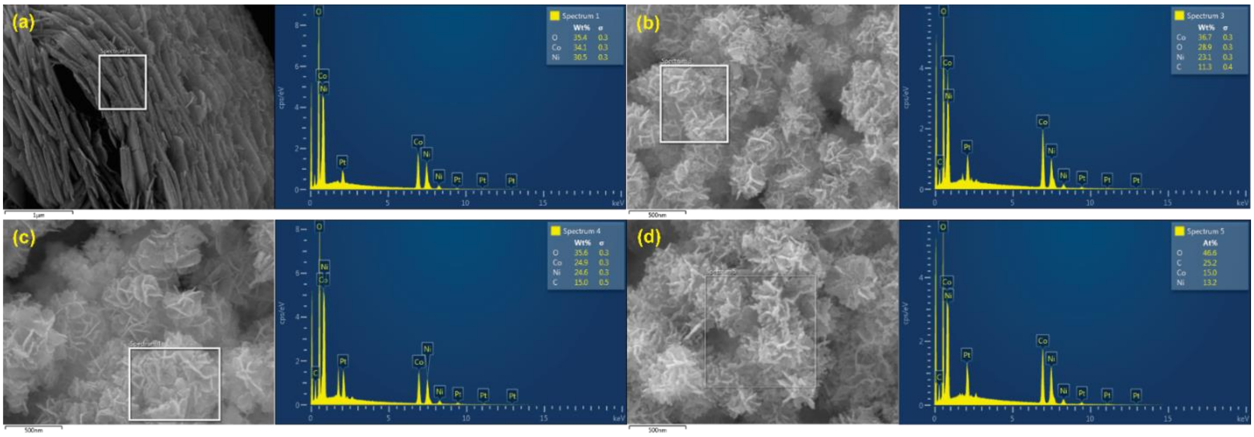


Figure 2. FE-SEM affiliated EDX spectrum of different samples a) $NiCo_2O_4$-1 b) $C@NiCo_2O_4$-2 c) $C@NiCo_2O_4$-3 d) $C@NiCo_2O_4$-4.

The X-ray diffraction studies were carried out in order to identify the purity of phase formation and crystallinity of prepared sample. Observed maximum intensity peak is revealing prepared $NiCo_2O_4$ and C@$NiCo_2O_4$ have a fine face-centered cubic structure and the same time it is well coordinated with JCPDS card no (20-0781). In Fig. 3a, the observed 2Ө angle peak at 18.9, 31.5, 36.3, 37.6, 43.1, 55.3, 58.7 and 64.6 correspond to the planes of 111, 220, 311, 222, 400, 422, 511 and 440 planes of spinel structured $NiCo_2O_4$. There is no discarded and additional peak even after the addition of carbon source. It indicates the successful synthetization of carbon coated $NiCo_2O_4$ without damaging crystal structure [7, 15]. XPS study was carried out to identify the elemental composition and oxidation states of the compound. As shown in Fig 3c, the observation of full XPS scanned peaks at 290ev, 520ev, 780ev and 870ev it confirms the presence of C 1s, O 1s, Ni 2p and Co 2p respectively. It indicates the valence state and elemental composition of C@$NiCo_2O_4$-3 [35].

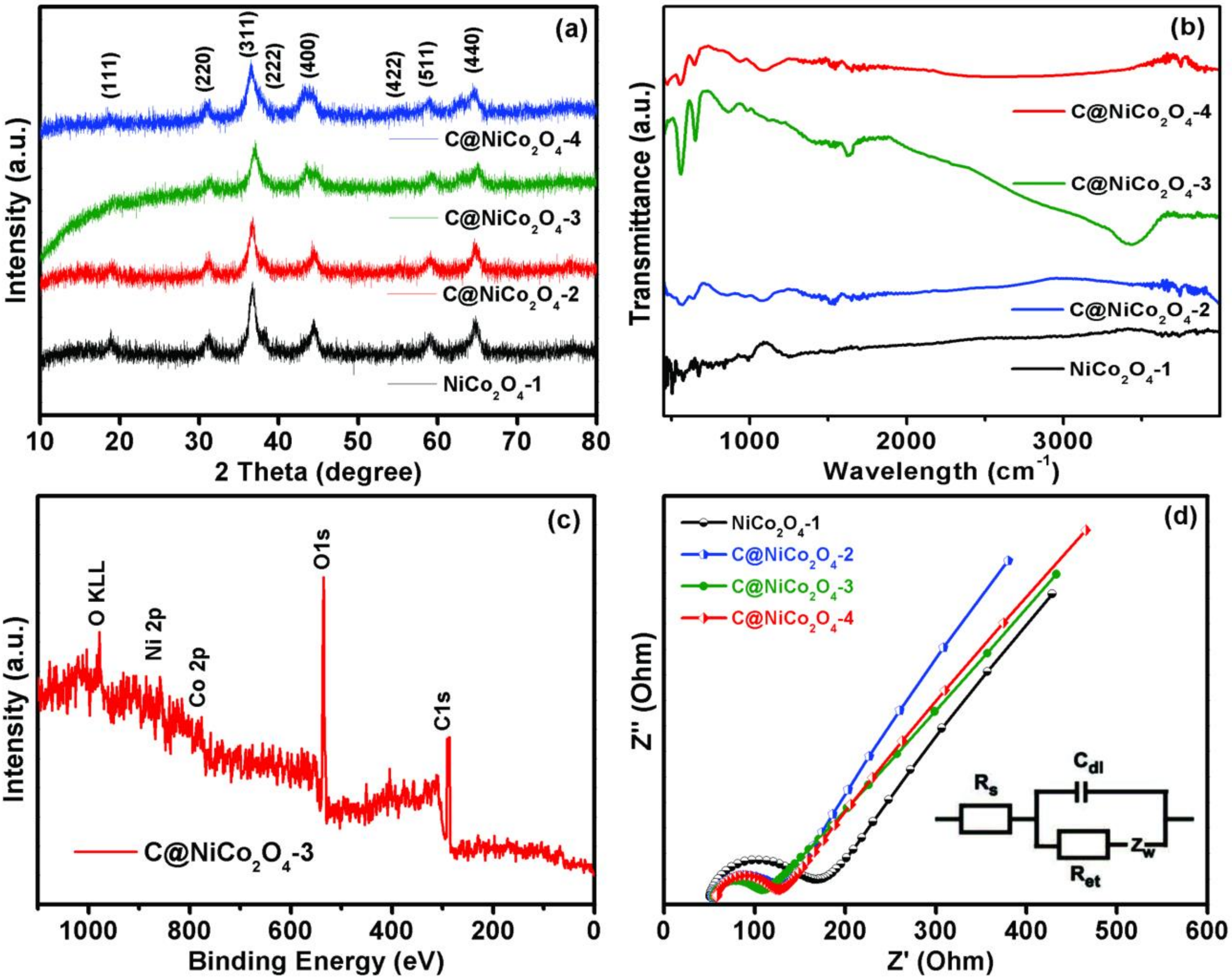


Figure 3. Physiochemical studies (a) XRD pattern (b) FTIR spectrum of $NiCo_2O_4$ and C@$NiCo_2O_4$ samples. (c) XPS spectra of full ranges C@$NiCo_2O_4$-3. (d) EIS spectrum of $NiCo_2O_4$ and C@$NiCo_2O_4$ samples.

The presence of the functional groups was considered as the important factor in the sensing of electroactive material because it often influences the electrochemical performance and wettability of the material. In order to identify the functional groups, FTIR analysis was carried for all the prepared sample. In fig. 3b, the observation of peaks at 553, 645 cm^{-1} for all the samples belongs to Ni-O and Co-O metal oxygen stretching vibrations in $NiCo_2O_4$. Additionally, there were two more broad and sharp peaks observed at 3413 and 1628 cm^{-1} respectively. It was attributed to the stretching vibrations mode of C=O, COOH and adsorbed water on the surface of carbon-coated $NiCo_2O_4$. Some more additional peaks were also arising when adding carbon source to the pristine material due to the hydroxyl, carboxyl and carbonyl functional groups, it confirms the formation of carbon on $NiCo_2O_4$ [36].

3.1 Electrochemical performance of $NiCo_2O_4$ and C@$NiCo_2O_4$

Electrochemical performance of pristine and carbon coated $NiCo_2O_4$ modified GCE were studied through cyclic voltammetry (CV) in 0.1 M KCL electrolyte at 50 mV s^{-1}. Fig 4a shows the obtained CV curve for all the prepared samples exhibited EDL (Electric double layer) behavior without any redox peaks. In the neutral electrolyte, ions are adsorbed on the electrode surface only and there was no electron transfer in-between modified electrode and electrolyte. Among all the obtained CV curve Pristine $NiCo_2O_4$ shows lesser area than the carbon coated $NiCo_2O_4$ at the same time when increasing melamine concentration (0.5, 1, 1.5 M) cv curve also increase due to as already mentioned in SEM image (fig. 1a) pristine $NiCo_2O_4$ particle has stacked layer, when start to add melamine in to pristine material stacked layers aligned into different direction this kind of changes increase the electrochemical exposer area of the material. C@$NiCo_2O_4$-3 shows maximum current area than other carbon-coated sample. Above 1 M melamine concentration may lead to morphology and structural changes, so CV curve of C@$NiCo_2O_4$-4 has a little bit lower than C@$NiCo_2O_4$-3. EDL behavior of all carbon coated samples strongly evidences the $NiCo_2O_4$ has surface coated carbon and that carbon influence the electrochemical performance by increasing the CV current area.

Electrochemical impedance spectroscopy reveals that the intrinsic electron transfer properties of prepared samples. As shown in Fig 3d, the Nyquist plot of $NiCo_2O_4$-1, C@$NiCo_2O_4$-2, C@$NiCo_2O_4$-3 and C@$NiCo_2O_4$-4 in the high-frequency region shows semicircle which indicates that the electron charge transfer resistance (R_{et}) of the electroactive material and linear straight line in low-frequency region indicates the diffusion controlled process. EIS validate the CV results pristine material has high charge transfer resistance (around 170 ohms) than other C@$NiCo_2O_4$. Carbon coated materials C@$NiCo_2O_4$-3, C@$NiCo_2O_4$-4 and C@$NiCo_2O_4$-2 exhibited low charge transfer resistance of 50 ohm, 65 ohm and 83 ohm respectively due to $NiCo_2O_4$ and surface coated-carbon synergistically give low electron transfer resistance. Basically, The carbon has high electrical conductivity individually and then the enhancement of electrical conductivity due to the inherent contribution of $NiCo_2O_4$ flower and surface coated carbon. CV and EIS show the C@$NiCo_2O_4$-3 modified GCE exhibits the good electrochemical performance among other materials [37, 38].

3.2 Electrochemical oxidation of sulfite

In order to analyze the electrocatalytic efficiency of all prepared materials of the modified GCE, CV studies were carried out in 0.1 M KCl neutral solution at the scan rate of 50 mVs^{-1}. Fig 4b shows the CV curve results of sulfite oxidation of completely irreversible redox peaks in between 0.4 to 0.6 V for pristine and carbon coated $NiCo_2O_4$ modified electrodes. The C@$NiCo_2O_4$-3 exhibits superior electrocatalytic performance by the earlier oxidation of sulfite into sulfate at 0.42 V with high oxidation peak current than C@$NiCo_2O_4$-2, C@$NiCo_2O_4$-4. When compared to the bare GCE, C@$NiCo_2O_4$-3 modified electrodes were observed the sulfite oxidation of potential earlier. As per expected results, the fine morphology and carbon coating of electrode material have enhanced the electrocatalytic activity and electronic conductivity of C@$NiCo_2O_4$-3. C@$NiCo_2O_4$-3 induces the sulfite oxidation of SO^{-2}_{3} to SO^{-2}_{4} at 0.42 V due to it has different directionally oriented fine nanosheets and surface coated carbon layer, it also encourage the prior detection of sulfite. The possible irreversible sulfite oxidation reaction is given below [39].

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^- \qquad - (1)$$

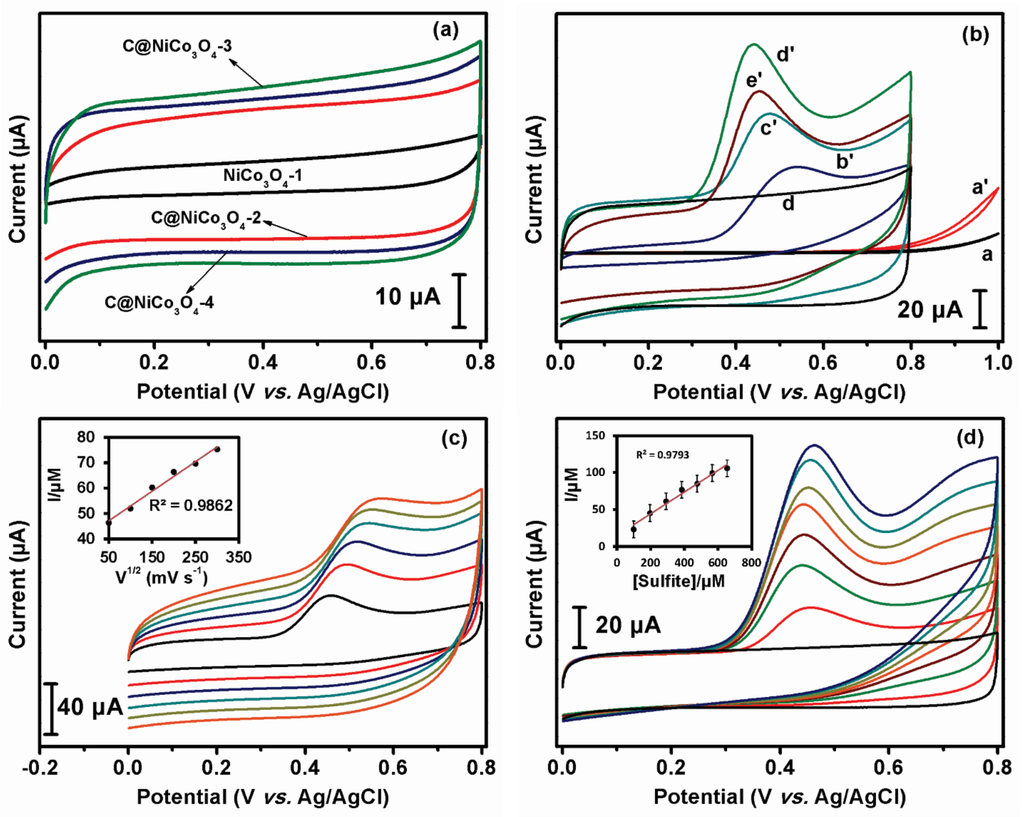


Figure 4. (a) CV profile of different modified electrode in N_2 statured 0.1 M KCl electrolyte at scan rate of 50 mV s^{-1}. (b) CV profile different modified electrode was studied at presents and absence of sulfite (196 µM) in 0.1 M KCl at a scan rate of 50 mV s^{-1}. (c) CV profile different scan rate in the presents of sulfite (196 µM) in N_2 statured 0.1 M KCl electrolyte. (Inset: different scan rate *vs*. the corresponding response peak current plot). (d) CV profile different concentration of sulfite (99-640 µM) in N_2 statured 0.1 M KCl at a scan rate of 50 mV s^{-1}. (Inset: different concentration of sulfite *vs*. corresponding peak current plot).

Through varying the sweep rate in CV, it reveals the electrochemical kinetics of diffusion control at the modified electrode. Fig 4c shows the CV curve of different sweep rate in 196 µM when increasing the sweep rate gradually oxidation peak current also increases with a slight sleep of oxidation potential and it reveals the diffusion limitation of the C@$NiCo_2O_4$-3 modified electrode. However, inset (Fig. 4c) correlation coefficient (R^2 = 0.9862) conforms the linear increment of the peak current of C@$NiCo_2O_4$-3 against sweep rate and diffusion controlled.

Meanwhile choosing the concentration of analyte for observing the effectiveness of sulfite detection by using optimized C@$NiCo_2O_4$-3 is important. When increasing the concentration of sulfite from 99 to 640 µM, the peak current also linearly increased that is shown in Fig. 4d. Inset plot in Fig 4d exhibits good linearity (with the correlation coefficient of R^2 = 0.9793) for the different concentration of sulfite *vs.* corresponding peak current plot. Sensitivity, linear range and limit of detection are essential parameters to scale efficiency of the electrochemical sensor. So here we have used a Chronoamperometry technique to measure the listed parameters because it has higher sensitivity to detect low current than cyclic voltammetry [30]. The amperometric technique was carried out in the continuous stirring condition of C@$NiCo_2O_4$-3 modified GCE (1200 rpm) at the optimized potential of 0.42 V in 0.1 M KCl solution by adding a different concentration of sulfite. Fig 5 depicts the stable and stepwise increment of oxidation current of the modified electrode when increasing the sulfite concentration. Inside Fig 5 maximized image displays the increment of current from the steady state even for very low concentration (0.3uM) it truly agrees with above-discussed results of C@$NiCo_2O_4$-3, due to the enhancement of electrical conductivity through synergistic effect between the intrinsic and extrinsic contribution of NiCo2O4 and Carbon respectively.

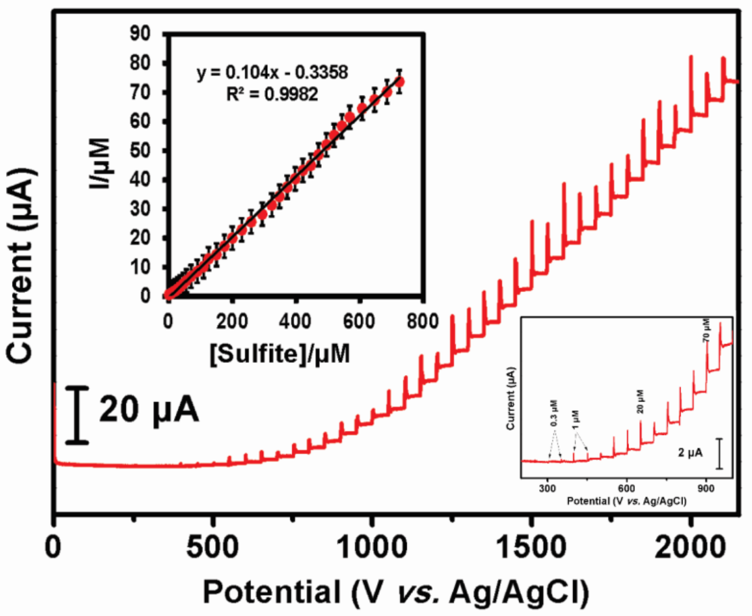


Figure 5. Amperometric profile for various concentration of sulfite in N_2 statured 0.1 M KCl electrolyte. Applied potential: +0.4 V; rpm: 1200. (Inset: different concentration of sulfite *vs.* corresponding response current plot).

The linear equation Y=0.104X-0.3358 (inset Fig 5) shows the detection linearity of C@$NiCo_2O_4$-2 against different concentration with the correlation coefficient of R^2 = 0.9982. Calculated sensitivity and low limit of detection are quite comparable with previously reported values (shown in table 1), the obtained values are 3.59 µA mM^{-1} cm^{-2} and 0.05 µM respectively. C@$NiCo_2O_4$-3 could detect in the broad range of sulfite with a linear range of 0.3 µM to 724 µM. Above mentioned amperometric value again suggest the prepared C@$NiCo_2O_4$-3 has efficient electrocatalytic properties than other carbon coated samples.

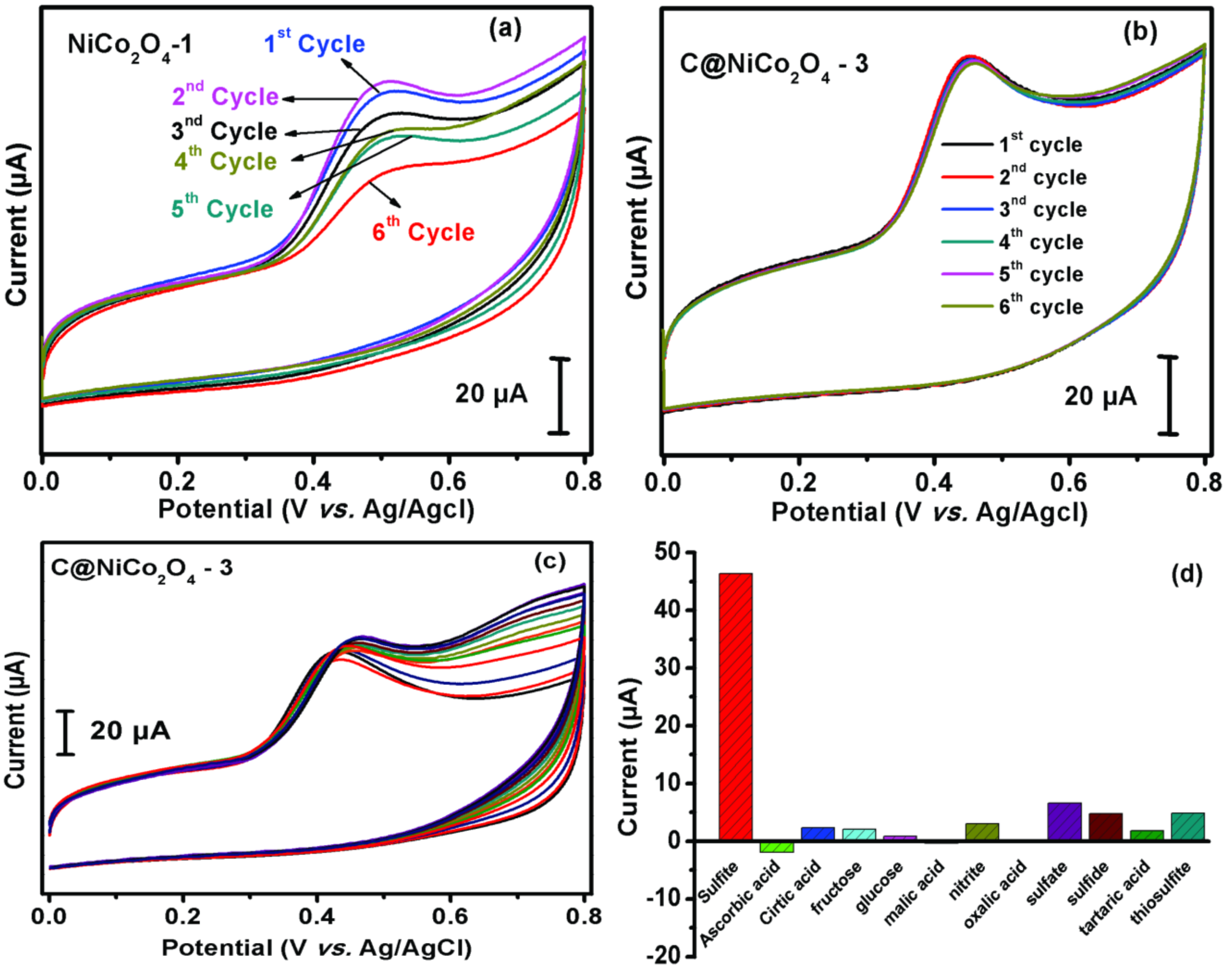


Figure 6. Cyclic Voltammetry curve of repeatability (a) without carbon coated material, (b) carbon coated material six-time repeated with 196 µM sulfite concentration in 0.1 M KCl electrolyte at 50 mVs^{-1}. (c) CV profile of interference studies at different analyte and (d) corresponding current response bar diagram.

The stable output current is a crucial factor in the sense of electrochemical sensor since if any variation in output current affects the accurate quantification of the analyte. Mainly this problem happens by degradation and structural changes of electrode material. So many research groups $NiCo_2O_4$ have been utilized as an electrode material to detect different analyte still $NiCo_2O_4$ exhibits unstable action due to the dispersion of material and structural changes in buffer solution and analyte

[2, 12, 35, 37, 40]. In order to resolve this kind of problem carbon was coated on $NiCo_2O_4$ using melamine as carbon precursor by the simple hydrothermal method. The output current of repeated action of pristine carbon coated $NiCo_2O_4$-1, C@$NiCo_2O_4$-3 modified GCE single electrode is giving stable output current for six-time repeated experiment with only 4% loss of its initial current when compare pristine material has loss of 43% initial current. When direct exposer of $NiCo_2O_4$-1 into buffer and analyte solution during electrocatalytic reaction material starts to lose its original phase and integrity due to external reaction degrade and dispersion. But in case of C@$NiCo_2O_4$-3 coated carbon layer is preventing from all problems additionally enhance the electrical conductivity because carbon has so many advantages like chemical inertness, high electrical conductivity [41], so the performance of C@$NiCo_2O_4$-3 is strongly evidenced the carbon coating has been improved the electrocatalytic efficiency with stable operation. CV curve (Fig 6 a, b) clearly depicts the when increasing repeated time gradual decrement of oxidation peak current of $NiCo_2O_4$-1 but carbon coated (C@$NiCo_2O_4$-3) $NiCo_2O_4$ exhibit stable peak current for more repeated times.

Selectivity and real sample analysis are essential than other experiments for the electrochemical sensor in the aspects of commercialization. Selectivity of C@$NiCo_2O_4$-3 was tested by using CV (Fig 6c) at 196 μM sulfite concentration with continuous addition of a lot of interference species in 0.1M KCl solution. Typically selectivity of nanomaterial is based on its real surface area, previous reports also suggest the when increasing the surface area selectivity also increase this is mainly due to the physical adsorption of selected species [40]. Fig 6d shows comparative bar diagram of sulfite oxidation peak current with 200 fold times added standard interference species mainly ascorbic acid, citric acid fructose, glucose, malic acid, oxalic acid and tartaric acid. During interference study negligible peaks current only observed for standard species. In another hand when injecting sulfur-based compounds like sulfate, sulfide and thiosulfate CV curve shows the very low current response of them due to all are sulfur groups otherwise C@$NiCo_2O_4$-3 reveals higher selectivity with a more accessible surface area of sulfite by nanoflower.

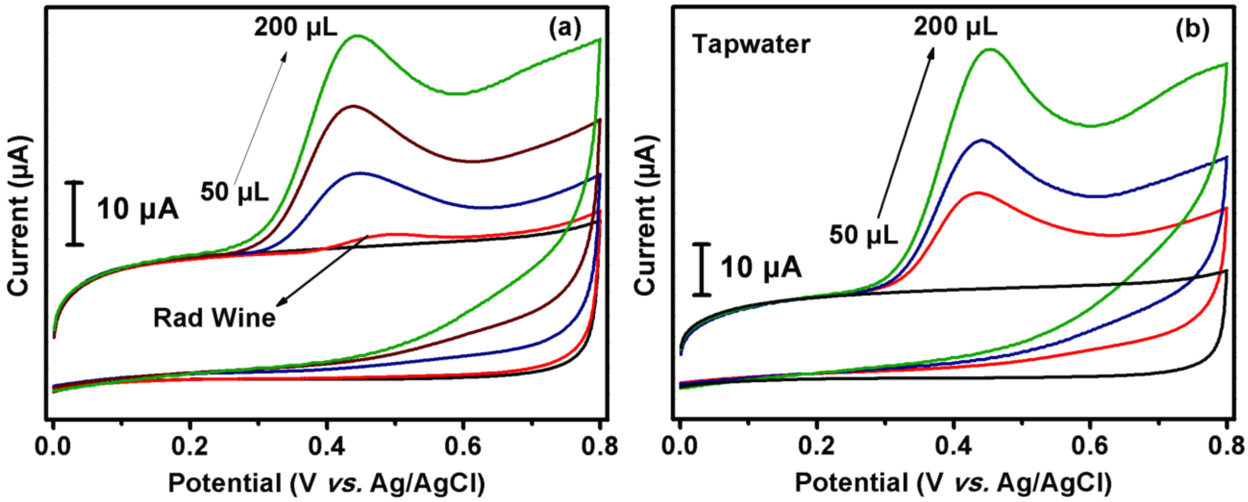


Figure 7. CV profile of the real sample analysis (standard addition method) of sulfite and (a) wine (b) tape water in N_2 statured 0.1 M KCl electrolyte at a scan rate of 50 mV S^{-1}.

To analyze the detection ability of C@$NiCo_2O_4$-3 in real time application red wine and local tape water was taken. By using CV C@$NiCo_2O_4$-3 modified electrode was tested, for each time 50, 100, 150, 200 µL was added by standard addition method. For every addition of real sample CV curve shows (Fig 7 a, b) well-matched oxidation peak with above CV study around at 0.43 V. this indicates the prepared C@$NiCo_2O_4$-2 has the capability to detect sulfite when present in natural substances and it is ready to come as a commercial electrochemical sensor.

Table 1. Analytical performance of amperometric electrochemical sensors for sulfite detection.

Electrode type	Sensitivity (µA $mM^{-1}cm^{-2}$)	Linear range (µM)	LOD (µM)	Working potential (V)	Reference
CNTs-PDDA-AuNPs/GCE	0.80	1.2–2500	0.4	0.40	22
NiPCNF/Al	0.13	4.0–200	3.0	0.65	16
CuHCF/CNT/CPE	0.17	6.2–620	5.0	0.55	15
FeHCF(PB)/GCE	2.18	up to 4000	80	0.85	11
[Ru(bpy)(tpy)Cl]PF_6	6.0	3.0–80	2.86	0.80	10
Copper-salen	–	4.0–69	1.2	0.45	9
PhSPCE	1.33	7.5–2500	3.5	0.40	8
C@$NiCo_2O_4$	3.57	0.3–724	0.05	0.42	This work

4. CONCLUSION

Carbon-coated Nickel cobaltite was successfully prepared by simple hydrothermal method and XRD, XPS, FTIR, SEM, and EDX are confirmed it has good physiochemical properties. In carbon coated $NiCo_2O_4$ primarily melamine has acted as carbon source additionally it is changed nanosheet bundle into nanoflower structure by the opening of nanosheet bundle with large accessible surface area compare to pristine $NiCo_2O_4$-1. Electrochemical performance of $NiCo_2O_4$ and C@$NiCo_2O_4$ has evaluated by cyclic voltammetry and amperometric technique and the modified electrodes have been shows the well electrocatalytic activity by oxidizing sulfite in 0.1 M KCl. Among, all carbon coated samples C@$NiCo_2O_4$-3 exhibited greater electrocatalytic activity by earlier oxidation of sulfite at 0.42 V. carbon coating is enhanced the performance of C@$NiCo_2O_4$-3 with good sensitivity (3.59 µA mM^{-1} cm^{-2}), low limit of detection (0.05 µM) and linear range (0.3 to 724 µM). Finally, electrochemical studies confirmed the carbon coated $NiCo_2O_4$ is promising electrode material for a real time electrochemical sensor to stable operation.

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