Hydrothermally synthesized Nickel cobalt oxide for bifunctional electrochemical supercapacitor and nonenzymatic glucose biosensor

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Abstract

Herein, various nickel cobalt oxide nanostructures with different Ni concentrations are prepared via hydrothermal route and then calcination process for electrochemical supercapacitor as well as nonenzymatic glucose biosensor. The electrode synthesized on carbon cloth using $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$ nanosheet-like morphology showed a maximum 516.51 F g^{-1} specific capacitance at 10 mV s^{-1} scan rate and the cyclic stability of 87.7% over 2000 GCD cycles. The electrode prepared with $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$ on CC offered a linear response from 0 to 0.3 mM glucose concentration and exhibited a maximum of $759.5 \mu\text{A mM}^{-1} \text{ cm}^{-2}$ glucose sensitivity.

1. Introduction

Nowadays, human beings have suffered from problems such as deficiency of fossil fuels, global warming, and pollution. Hence, it is essential to produce energy from renewable sources Like solar, tide, and wind. Also, low-cost, environmentally friendly, advanced energy storage and conversion devices must store energy harvested from renewable resources ¹⁻⁴. There are different energy storage devices such as conventional capacitors, biofuel, lithium ions batteries (LIBs), and supercapacitors ⁵⁻⁹. Supercapacitors, also called electrochemical supercapacitors, are the most desirable candidates for energy storage. Their unique electrochemical properties like high power density, excellent coulombic efficiency, and high cyclic stability make them compatible with other energy storage devices. Still, supercapacitors suffered from low energy density as compared to LIBs. So, to improve the energy density of supercapacitors, efforts have been made to develop novel electrodes with suitable synthesis strategies ¹⁰⁻¹⁴.

The different conducting polymers ¹⁵, transition metal oxides, and transition metal hydroxides such as Co_3O_4 ¹¹, NiO ¹⁶, $\text{Co}(\text{OH})_2$ ¹⁷, $\text{Ni}(\text{OH})_2$ ¹⁸, RuO_2 ¹⁹, MnO_2 ²⁰ has been widely studied as an electrode for pseudocapacitors. The transition metal oxides deliver higher specific capacitance as compared to conducting polymers due to multi-electron redox reactions. In addition, ternary metal oxides, because of their better electrical conductivity and rich redox-active sites, shows better supercapacitor performance than single metal oxide ²¹. Spinel nickel cobalt oxide (NiCo_2O_4) has been widely used as high-performance capacitive electrode material in recent years. It shows better electrical conductivity, relatively lower electron transport activation energy, and better electrochemical activity than cobalt oxide (Co_3O_4) and nickel oxide (NiO) ^{22,23}. This high electrical conductivity and improved specific capacitance of NiCo_2O_4 are because of contributions from both the Co and Ni ions with diverse valence states.

Researchers have made many efforts to enhance electrochemical performance by developing nickel cobalt oxide with different morphologies. Waghmode et al. ²⁴ synthesized NiCo_2O_4 nanoflowers by chemical bath deposition method and observed capacitance was 610 F g^{-1} at 1 mA cm^{-2} . Ma et al. ²⁵, with the solution precursor thermal spray method, developed NiCo_2O_4 hollow microspheres, which showed specific capacitance 902 F g^{-1} at 1 A g^{-1} . Qi et al. ²⁶ synthesized NiCo_2O_4 hollow microspheres by a

hydrothermal method which showed specific capacitance 720 F g^{-1} at 2 A g^{-1} . Saravanakumar et al.²⁷ synthesized NiCo_2O_4 nanoparticles via hydrothermal route and observed specific capacitance was 294 F g^{-1} at 1 A g^{-1} . Uke et al.²⁸ synthesized NiCo_2O_4 nanomorphs by hydrothermal method and observed specific capacitance was 479 F g^{-1} with better retention.

In the medical industries, quality control in food and clinical diagnosis of diabetes; rapid, accurate, and sensitive detection of glucose is essential^{29,30}. Recently, sensitive and selective enzyme-based sensors have been studied for glucose sensing. But, they cannot be reused for continuous glucose detection. They suffer from low stability, which limits their use in actual application^{31,32}. The other method, i.e., nonenzymatic glucose biosensing, exhibited high stability, sensitivity, and reproducibility. Qin et al.³³ developed NiCo_2O_4 nanowires with the help of hydrothermal and calcination treatment. The prepared glucose sensor shows $72.4 \text{ mM mM}^{-1} \text{ cm}^{-2}$ glucose sensitivity and 0.37 mM detection limit. Hussain et al.³⁴ prepared NiCo_2O_4 nanoneedles on Nickel Foam exhibited a sensitivity of 91.34 mV/decade with a response time less than 10 s . Yang et al.³⁵ synthesized hollow nanorods of NiCo_2O_4 with the help of sacrificial template accelerate hydrolysis method achieved $1685.1 \text{ mM mM}^{-1} \text{ cm}^{-2}$ glucose sensitivity. Ma et al.³⁶ developed NiCo_2O_4 nanowrinkles on graphene oxide sheets with hydrothermal route achieved glucose sensitivity of $548.9 \text{ mM mM}^{-1} \text{ cm}^{-2}$.

In the present investigation, the different nickel cobalt oxide nanostructures by varying concentrations of Ni in cobalt oxide are prepared by the hydrothermal route and studied for both supercapacitor and glucose biosensing applications. The electrodes are synthesized using a flexible carbon cloth (CC) current collector with a simple doctor blade method. The synthesized $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$ nanosheets exhibited 516.51 F g^{-1} specific capacitance at 10 mV s^{-1} with capacity retention of 87.7% over 2000 cycles. At the same time, $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$ nanosheets showed maximum $759.5 \mu\text{A mM}^{-1} \text{ cm}^{-2}$ glucose sensitivity with a linear response from 0.0 to 0.3 mM glucose concentration.

2. Experimental

A. Preparation of different Nickel cobalt oxide powders:

The nickel cobalt oxide powders with different Ni percentages were synthesized by the hydrothermal route and then calcination. In a synthesis of Co_3O_4 , $0.1 \text{ M Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.2 M of urea were added in Double distilled water (DDW). NH_3 was added to the solution dropwise up to $\text{pH} = 11$ and stirred for 30 min . Afterward, the whole solution was poured into a Teflon liner (100 mL), fitted in stainless-steel autoclave and reaction carried out at 180°C for 18 h . Then, the autoclave was cooled to room temperature, and reaction products were cleaned with DDW and ethanol many times and dried at 60°C oven for 12 h . Lastly, the prepared powder was calcinated at 400°C for 2 h . Similarly, powders with different Ni concentrations were synthesized by adding a different percentage of Ni as 0% , 10% , 20% ,

30%, and 40% in Co_3O_4 . Based on the various percentages of Ni precursor, the stoichiometries are observed Co_3O_4 , $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$, $\text{Ni}_{0.6}\text{Co}_{2.4}\text{O}_4$, $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$, and $\text{Ni}_{1.2}\text{Co}_{1.8}\text{O}_4$, respectively.

B. Preparation of electrode

In an ultrasonication bath, a piece of CC (2 cm × 1 cm) was cleaned with ethanol, acetone, and DDW each for 10 min respectively, and dried overnight at 60 °C in the oven. The actual electrode was prepared by mixing prepared powders (active material), PVDF as a binder, and a carbon black ratio of 80:10:10. Then sufficient amount of NMP solvent was mixed to obtain a uniform slurry. Then the prepared slurry was coated on CC (1 cm × 1 cm) and subjected to 80 °C in a hot air oven for 12 h. These prepared electrodes were used for electrochemical supercapacitor and nonenzymatic glucose biosensor study. The experimental procedure can be presented in Fig. 1.

XRD pattern of prepared powders recorded using a Bruker D2 phaser tabletop model under Cu Ka radiation. FTIR was taken by Lambda-7600, Australia. The morphology was analyzed using FE-SEM from the Mira-3, Tescan, Brno-Czech Republic. Biologic SP-300 electrochemical workstation used for electrochemical supercapacitor and glucose biosensor study.

3. Results And Discussion

3.1 XRD study

Fig. 2 (A) presents the XRD spectra of different Nickel cobalt oxide nanostructures. The observed d-spacing values in XRD spectra are associated with standard JCPDS card 01-080-1543 for Co_3O_4 and 01-073-1702 after adding different Ni concentrations. The peaks are observed at an angle, 64.98, 59.19, 44.68, 36.79, 31.16, 18.94° which applied to the cubic structure and assigned to the (440), (511), (400), (311), (220), and (111) crystal planes respectively. The crystallite size is calculated by using Scherer's formula^{7,37}. The calculated values for average crystallite size are 34.18, 36.61, 43.10, 30.96, and 34.18 nm for Co_3O_4 , $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$, $\text{Ni}_{0.6}\text{Co}_{2.4}\text{O}_4$, $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$, and $\text{Ni}_{1.2}\text{Co}_{1.8}\text{O}_4$, respectively.

3.2 FTIR study

The different Nickel cobalt oxide powders were further characterized by the FT-IR study. Fig. 2 (B) presents the FTIR spectra of all synthesized nickel cobalt oxide powders. The FTIR spectra display two sharp peaks at about 661 cm^{-1} and 565 cm^{-1} which are originated from Co-O bonds (stretching vibrations), confirms the formation of Co_3O_4 ^{38,39}. As the percentage of Ni increases, these two peaks shift towards a higher wavenumber. The corresponding change in the peak is mentioned in supplementary information Table S1. The relatively weak peaks at about 1632 and 3432 cm^{-1} are associated with O-H bending and stretching mode of vibration of water⁴⁰⁻⁴².

3.3 FE-SEM study

Fig. 3 shows FE-SEM pictures and EDS analysis of different nickel cobalt oxide powders. The Co_3O_4 in Fig. 3 (A) shows nanosheets like nature. As the different percentages of Ni are added into Co_3O_4 , surface modifications are observed. In Fig. 3 (B), the nanosheet-like morphologies are observed, which are merged. As the percentage of Ni increases, the nanosheets are incorporated a lot in Fig. 3 (C). The flakes are started covered with nanoparticles in Fig. 3 (D), and finally, the number of nanoparticles increased as shown in Fig. 3 (E) corresponding to the $\text{Ni}_{1.2}\text{Co}_{1.8}\text{O}_4$. Fig. 3 (F) shows the EDS spectra of $\text{Ni}_{1.2}\text{Co}_{1.8}\text{O}_4$, which confirms the presence of Ni, Co, and O. Fig. 3 (G-I) presents the elemental distribution of Ni, Co, and O, respectively.

3.4 EIS study

The electrochemical behavior at the electrode-electrolyte interface was studied by using the EIS study. Fig. 4 presents the EIS study of synthesized Co_3O_4 , $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$, $\text{Ni}_{0.6}\text{Co}_{2.4}\text{O}_4$, $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$, and $\text{Ni}_{1.2}\text{Co}_{1.8}\text{O}_4$ electrodes. EIS spectra were recorded within 1 MHz to 0.1 Hz frequency range in 1 M KOH electrolyte at applied potential 20 mV. Fig. 4 (A) presents the Nyquist plots of Co_3O_4 , $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$, $\text{Ni}_{0.6}\text{Co}_{2.4}\text{O}_4$, $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$, and $\text{Ni}_{1.2}\text{Co}_{1.8}\text{O}_4$ electrodes. The Inset of Fig. 4 (A) shows the corresponding fitted circuit diagram. The solution resistance (R_s) values estimated from Nyquist plot for Co_3O_4 , $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$, $\text{Ni}_{0.6}\text{Co}_{2.4}\text{O}_4$, $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$, and $\text{Ni}_{1.2}\text{Co}_{1.8}\text{O}_4$ electrodes are 0.08, 0.37, 0.36, 0.02, and 0.15 W cm^{-2} . The charge transfer resistance values for Co_3O_4 , $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$, $\text{Ni}_{0.6}\text{Co}_{2.4}\text{O}_4$, $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$, and $\text{Ni}_{1.2}\text{Co}_{1.8}\text{O}_4$ electrodes are 88.81, 91.51, 109.10, 79.51, and 90.47 W cm^{-2} respectively. The lower R_{ct} and R_s values reveal the better electrical conductivity and good adhesion of coated material with current collector⁴³. The different EIS parameters are mentioned in supplementary information Table S2. Fig. 4 (B) presents the Bode plot of Co_3O_4 , $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$, $\text{Ni}_{0.6}\text{Co}_{2.4}\text{O}_4$, $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$, and $\text{Ni}_{1.2}\text{Co}_{1.8}\text{O}_4$ electrodes, respectively.

3.5 Electrochemical supercapacitor study

The three-electrode system with SCE as a reference electrode, platinum wire counter electrode, and prepared CC electrodes as a working electrode is used to study electrochemical supercapacitor performance. The electrochemical performance is studied in 1 M KOH electrolyte.

Fig. 5 A presents the cyclic voltammetry (CV) curves of all nickel cobalt oxide electrodes studied at a 10 mV s^{-1} scan rate. The maximum capacitance values estimated from CV curves are 189.31, 204.22,

220.63, 516.51, and 312.32 F g⁻¹ for Co₃O₄, Ni_{0.3}Co_{2.7}O₄, Ni_{0.6}Co_{2.4}O₄, Ni_{0.9}Co_{2.1}O₄, and Ni_{1.2}Co_{1.8}O₄ electrodes, respectively. All CVs, along with different scan rates, are mentioned in Fig. S1 (A-E). From the graphs in Fig. S1, it is clear that with an increase in scan rate, the area under the curve increases as the current drawn increases with the voltage in the CV graph. But the increase in scan rate limits the interaction time between electrolyte and electrode. This limited-time interaction between electrode and electrolyte also limits the utilization of the active surface area of the electrode. Hence specific capacitance decreases with the increase of scan rate ⁴⁴.

The galvanostatic charge-discharge curves are displayed in fig. 5 B of different nickel cobalt oxide electrodes studied at current density 3 mA cm⁻². The maximum specific capacitance values estimated from GCD curves are 89.10, 101.27, 165.38, 455.27, and 337.01 F g⁻¹ for Co₃O₄, Ni_{0.3}Co_{2.7}O₄, Ni_{0.6}Co_{2.4}O₄, Ni_{0.9}Co_{2.1}O₄, and Ni_{1.2}Co_{1.8}O₄ electrodes, respectively. All GCD study with various current densities is mentioned in Fig. S2 (A-E). The cyclic stability is measured for the Ni_{0.9}Co_{2.1}O₄ electrode as it exhibited a higher capacitance value than other nickel cobalt oxide nanostructured electrodes. The observed stability for the Ni_{0.9}Co_{2.1}O₄ electrode is 87.7% over the 2000 charging-discharging cycles as depicted in Fig. 5 C. Inset image of Fig. 5C shows the first and last charging and discharging cycles. The higher specific capacitance and stability of Ni_{0.9}Co_{2.1}O₄ electrode may be due to micro sheets covered nanospheres like morphology. The micro sheets and nanosphere morphology provide maximum surface area so that the interaction between electrode and electrolyte becomes easier, enhancing the specific capacitance value. The calculated specific capacitance from CV vs. scan rate is mentioned in fig. 5 D. In contrast, the variation of specific capacitance vs. current density is mentioned in fig. 5 E. Fig. 5 F presents the Ragone plot. The maximum energy density for the Ni_{0.9}Co_{2.1}O₄ electrode is 15.81 Wh kg⁻¹ (at 0.75 kW kg⁻¹ power density). The comparison of supercapacitor performance of present work and previously reported work is mentioned in Table. 1.

3.6 Nonenzymatic glucose biosensing study

Here the same three-electrode system is used for the glucose sensing study except for 0.1 M NaOH electrolyte. Fig. 6 (A-E) presents the CVs of Co₃O₄, Ni_{0.3}Co_{2.7}O₄, Ni_{0.6}Co_{2.4}O₄, Ni_{0.9}Co_{2.1}O₄, and Ni_{1.2}Co_{1.8}O₄ electrodes in the absence of glucose (red) and in the presence of 1.0 M glucose (blue). Fig. 7 (A-E) presents the CV curves of Co₃O₄, Ni_{0.3}Co_{2.7}O₄, Ni_{0.6}Co_{2.4}O₄, Ni_{0.9}Co_{2.1}O₄, and Ni_{1.2}Co_{1.8}O₄ electrodes at different concentration of glucose (0.0, 0.2, 0.4, 0.6, 0.8, 1.0 M). Here we can observe that for all samples, peak currents are increased after the addition of glucose. The increase in the peak currents is explained as follows ⁴⁵,

During the oxidation, Ni^{2+} and Co^{2+} ions present in the NiOOH and CoOOH compounds oxidize to Ni^{3+} and Co^{3+} with the release of two electrons (eq. 1-3). After adding glucose, the glucose molecules dissociate and are converted into gluconolactone with the release of two electrons (eq. 4). During reduction, the oxidized species Ni^{3+} and Co^{3+} reduce back to the Ni^{2+} and Co^{2+} by accepting electrons and returning to their original states. Fig. 8 (A-E) presents the CV of different nickel cobalt oxide electrodes in the presence of 1.0 M glucose at various scan rates ($10\text{--}100 \text{ mV s}^{-1}$). It can be seen that with scan rate, the anodic and cathodic peaks also increase. Fig. 9 (A-E) presents the chronoamperometry study (I vs. t) of each nickel cobalt oxide electrode at 0.4 V applied potential with the subsequent addition of 0.05 mM glucose into 0.1 M NaOH electrolyte. The inset of Fig. 9 (A-E) shows their calibration curves of Amperometric responses. The observed sensitivities for Co_3O_4 , $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$, $\text{Ni}_{0.6}\text{Co}_{2.4}\text{O}_4$, $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$, and $\text{Ni}_{1.2}\text{Co}_{1.8}\text{O}_4$ electrodes are 370.7, 759.5, 747.4, 557.7, 688.1 $\mu\text{A mM}^{-1} \text{ cm}^{-2}$, respectively. The Nyquist plots in the absence of glucose and in the presence of 1.0 mM glucose are shown in supplementary information Fig. S3. The estimated glucose-sensing parameters are given in Table 2. As shown in Fig. 10 (A-E), the selectivity of samples was examined by addition 0.2 mM glucose and other interfering species [0.0125 mM of uric acid (UA), Ascorbic acid (AA), Fructose (FR), Sucrose (SA), and Lactic acid (LA)]. All the electrodes showed a negligible effect of interfering species as compared to glucose. The response times for all prepared electrodes are mentioned in Fig. S4 (Supplementary data). The comparative glucose-sensing study of current work and previously reported work is mentioned in Table. 3.

4. Conclusion

In summary, the nickel cobalt oxide by varying Ni concentrations has been prepared by the hydrothermal method. The nanosheet like $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$ electrode exhibited 516.51 F g^{-1} specific capacitance at 10 mV s^{-1} and cyclic stability of 87.7% over 2000 galvanostatic charge-discharge cycles. Also, it showed an energy density of 15.81 Wh kg^{-1} at 0.75 kW kg^{-1} power density. The $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$ nanosheets on CC showed linear response from 0 to 0.3 mM glucose concentration and exhibited the highest glucose sensitivity of $759.5 \mu\text{A mM}^{-1} \text{ cm}^{-2}$. The overall study is a platform for the development of a flexible, high stability supercapacitor and reliable nonenzymatic glucose sensor.

Declarations

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Tables

Tables 1-3 are in the supplementary files section.

Figures

Figure 1

Schematic representation of overall experimental procedure.

Figure 2

Structural analysis of nickel cobalt oxide (A) XRD spectra and (B) FTIR of nickel cobalt oxide powders with different Ni concentrations.

Figure 3

Morphology of nickel cobalt oxide powders. (A-E) FE-SEM images of Co_3O_4 , $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$, $\text{Ni}_{0.6}\text{Co}_{2.4}\text{O}_4$, $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$, and $\text{Ni}_{1.2}\text{Co}_{1.8}\text{O}_4$ powders, respectively. (F) EDS image of $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$ powder. (G-I) Element distribution images of Ni, Co, and O, respectively.

Figure 4

EIS analysis of all nickel cobalt oxide powders. (A) Nyquist plot (B) Bode plot of different nickel cobalt oxide powders with different Ni concentrations. (c) Equivalent circuit diagram.

Figure 5

Supercapacitor study of nickel cobalt oxide powders with different Ni concentrations. (A) CVs of all nickel cobalt oxide electrodes on CC at 10 mV s^{-1} scan rate. (B) GCD study of different prepared electrodes at 3 mA cm^{-2} current density. (C) Cyclic stability of electrodes prepared by using $\text{Ni}_{0.9}\text{Co}_{2.1}\text{O}_4$ powder. Inset: First and last five cycles of GCD curves. (D) Estimated specific capacitance from CV vs. of scan rate. (E)

Specific capacitance calculated from GCD curve vs. applied current density. (F) Regone plot of different nickel cobalt oxide electrodes.

Figure 6

Behavior of different nickel cobalt oxide electrodes on CC with and without presence glucose. (A-E) CVs of Co3O4, Ni0.3Co2.7O4, Ni0.6Co2.4O4, Ni0.9Co2.1O4, and Ni1.2Co1.8O4 electrodes, respectively, with and without the presence of glucose.

Figure 7

(A-E) CV curves of Co₃O₄, Ni_{0.3}Co_{2.7}O₄, Ni_{0.6}Co_{2.4}O₄, Ni_{0.9}Co_{2.1}O₄, and Ni_{1.2}Co_{1.8}O₄ electrodes at different concentrations of glucose at 100 mV s⁻¹.

Figure 8

(A-E) CVs of Co₃O₄, Ni_{0.3}Co_{2.7}O₄, Ni_{0.6}Co_{2.4}O₄, Ni_{0.9}Co_{2.1}O₄, and Ni_{1.2}Co_{1.8}O₄ electrodes in the presence of 1.0 mM glucose at 10 to 100 mV s⁻¹ scan rate.

Figure 9

(A-E) Amperometric responses (I vs. t) of Co₃O₄, Ni_{0.3}Co_{2.7}O₄, Ni_{0.6}Co_{2.4}O₄, Ni_{0.9}Co_{2.1}O₄, and Ni_{1.2}Co_{1.8}O₄ electrodes at a 0.5 V potential with the addition of 0.05 mM glucose. Inset of each graph: calibration curves of chronoamperometric study]

Figure 10

(A-E) chronoamperometry study of (I vs. t) of Co₃O₄, Ni_{0.3}Co_{2.7}O₄, Ni_{0.6}Co_{2.4}O₄, Ni_{0.9}Co_{2.1}O₄, and Ni_{1.2}Co_{1.8}O₄ electrodes after successive addition of glucose and interference species [UA, AA, FR, SA, and LA].

Supplementary Files

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