Calcination Strategy for Scalable Synthesis of Pithecellobium-Type Hierarchical Dual-Phase Nanostructured Cu\textsubscript{x}O to Columnar Self-Assembled CuO and Its Electrochemical Performances

Kishor Kumar Sahu, Benjamin Raj, Suddhasatwa Basu, and Mamata Mohapatra*

ABSTRACT: The search for low-cost environmentally benign promising electrode materials for high-performance electrochemical application is an urgent need for an applausible solution for the energy crisis. For this, the present attempt has been made to develop a scalable synthetic strategy for the preparation of pure and dual-phase copper oxide self-hybrid/self-assembled materials from a copper oxalate precursor using the calcination route. The obtained samples were characterized by means of various physicochemical analytical techniques. Notably, we found that the BET surface area and pore volume of copper oxides measured by N\textsubscript{2} adsorption–desorption decrease with the elevation of calcination temperature. From the XRD analysis, we observed the formation of a Cu\textsubscript{2}O cubic phase at low temperatures and a CuO monoclinic phase at high temperatures (i.e., 450 and 550 °C). FTIR and RAMAN spectroscopy were employed for bonding and vibrational structure analysis. The self-assembled dual-phase copper oxide particle as a pithecellobium-type hierarchical structure was observed through SEM of the sample prepared at 350 °C. The surface morphological structure for the samples obtained at 450 and 550 °C was a bundle-like structure developed though columnar self-assembling of the particles. All the above techniques confirmed the successful formation of Cu\textsubscript{2}O/CuO nanoparticles. Afterward, the electrochemical properties of the as-synthesized copper oxides reinforced by introducing carbon black (10% wt) were explored via cyclic voltammetry, electrochemical impedance spectroscopy, and galvanometric charge–discharge analysis. The Cu\textsubscript{2}O system exhibits the maximum specific capacitance performance value of 1355 F/g, whereas in the CuO system (at 450 and 550 °C), it possesses values of 903 and 724 F/g at a scan rate of 2 mV/s. This study reveals that the electrochemical properties of Cu\textsubscript{2}O are better than those of the CuO nanoparticles, which could be ascribed to the high surface area and morphology. The present assessment of the electrochemical properties of the developed material could pave the way to a low-cost electrode material for developing other high-performance hybrid electrodes for supercapacitor or battery applications.

1. INTRODUCTION

The rational design of energy storage devices or platforms that shows excellent performance greatly depends on the electrode materials. Therefore, top priority has given to explore widely acceptable electrode materials for the development of cost-effective, safe, and high-capacitive, multidimensional mode of energy storage devices, which is desperately warranted for sustainable and green technology.\textsuperscript{1,2} Among all the energy storage devices, the electrochemical supercapacitors, either electrical double-layer capacitors (EDLCs) or pseudocapacitors are promising devices in the field of energy storage as they have a high power density, energy density, a rapid charge–discharge rate, and an excellent cyclic stability.\textsuperscript{3,4} For these advantages, emphasis has given to pure/binary or ternary oxides based on transition metals as one of the best candidate material.\textsuperscript{7–11} In this context, mostly ongoing R&D is focused on engineering an effective preparation method for manipulating surface activities, the crystal structure, and the morphology to obtain optimal electrochemical properties.\textsuperscript{12–17} Again, scalable synthesis and wide availability of the precursor metal ions along with their consistency in the supply chain are the major challenges for establishing the future emerging technology. Among them, copper-based oxides are significantly addressing most of the issues because of their worldwide available resources, being environmentally friendly, and...
possessing manipulative specific capacitance. To achieve its theoretical capacity, the pseudocapacitance of CuO is 1800 F/g and that of Cu2O is up to 2247 F/g. The electrochemical performance of copper oxide-based material was harmonized with the size- and shape-oriented morphologies such as nanoparticles, nanocubes, nanocages, nanowires, and polyhedrons developed by adopting various synthetic routes. Remarkable rate capacities are reported for the CuO-based electrode material with the assistance of other metal ions/oxides via facile synthesis methods. However, priorities are given for developing diversified nanostructures for copper oxide, hybridization with other oxides/organic materials rather than improvising the inherent properties of different copper oxide phases in combination, which will become strategic materials to develop high-performance composites to fulfill the urgent demand. Very few literature is found to be reported for the development of dual-phase composite electrodes for super capacitor applications based on different Cu2O. Although few large-scale syntheses of hybrid CuO/Cu2O nanoparticles via solid-state reaction such as the exploding wire technique have been reported, it is still challenging to develop such a material in a commercially economical and an environmentally benign scalable process. Herein, we have reported a facile procedure to synthesize stable dual-phase temperature-dependent CuO with superior specific capacitance than earlier reported pure CuO material in a three-electrode system.

2. RESULTS AND DISCUSSION

2.1. Physicochemicals and Morphological Characterization

The crystal structure and orientation of the prepared samples were investigated by the X-ray diffraction (XRD) pattern and are presented in Figure 1a. It is significant to note that the sharp and intense peaks reveal that the samples are of high crystallinity with a high degree of purity. Further, copper oxide (Cu2O and CuO) nanoparticles were prepared by thermal decomposition of CuC2O4. The XRD pattern of the metal oxide was studied within the diffraction angle of 30°–90°. The XRD profile of sample at 350 °C have diffraction peaks at 2θ angles of 29.58, 36.44, 42.32, 52.48, 61.40, 65.58, 69.62, 73.55, 77.41, and 84.98° and are well indexed with different hkl planes of (110), (111), (200), (211), (220), (221), (310), (311), (222), and (321), respectively. All the diffraction peaks are well-matched with the standard JCPDS card no. 01-078-2076 confirmed the formation of cubic structured Cu2O with a space group of P n3 M. The thermal oxidation of Cu2O to CuO was well matched with previously reported literature. In order to demonstrate the effect of annealing temperature over the metal oxide nanoparticles, it has been annealed at
three different (350, 450, and 550 °C) temperatures. The average crystallite size of the sample was calculated by the Debye Scherrer equation.

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]

where \( \lambda \) is the wavelength of X-ray radiation, \( \beta \) is the full width at half-maximum, \( D \) is the average crystallite size, and \( \theta \) is the diffraction angle. The average crystallite size and crystallinity of the metal oxide nanoparticles increase as the temperature of the sample increases, which might be due to the high degree of agglomeration. The average crystallite size of the samples was found to be 9, 13, and 14 nm at 350, 450, and 550 °C respectively. As the temperature increases, the collision of the particles increases to its maximum value and the particles coalesce with one another due to the atomic diffusion, which results in a decrease in the average crystallite size.34,35 The formation of Cu2O was confirmed due to the appearance of one extra peak at 2 theta 43°. It is the significant peak representing the successful formation of Cu2O nanoparticles.

The as-synthesized copper oxide with different temperatures was subjected to FTIR analysis to evaluate the chemical composition and to confirm the formation of copper oxide. The spectra of all the synthesized material were recorded at room temperature within the range of 400 to 4000 cm\(^{-1}\) as shown in Figure 1b. The peaks at approximately 2981, 2850, and 1697 cm\(^{-1}\) correspond to C–C stretching of the methylene group.36 The additional peaks observed at around 1094 cm\(^{-1}\) (C–O) and around ~3125 cm\(^{-1}\) are assigned to the C–O and O–H stretching frequency, which might be due to the presence moisture. The peaks at 816, 527, and 463 cm\(^{-1}\) can be assigned to Cu–O vibration, which confirms the existence of Cu2O and CuO in the final product. As it can be seen from the graph, the intensity of the peaks getting reduced and also the broad peaks observed at around 500 cm\(^{-1}\) might be due to the phase transition from CuO to Cu2O. To validate the FTIR results, RAMAN analysis of as-synthesized materials derived from the thermal decomposition of copper oxalate with different temperatures was performed and is presented in Figure 1c. The characteristic bands at 282, 326, and 518 cm\(^{-1}\) correspond to copper oxide.37 The two bands observed at 1055 and 2431 cm\(^{-1}\) could be attributed to the CO stretching mode of oxalate.38 The significant peaks at 282 and 326 cm\(^{-1}\) correspond to the Raman fingerprint signals from Ag and Bg modes of CuO, respectively, which have been well-matched with previous reported studies by Debbichi et al.39 and Volanti et al.40 When the sample was annealed at 450 and 550 °C, two smaller peaks (282 and 326 cm\(^{-1}\)) disappear and the intensity increased and widened at 518 cm\(^{-1}\). The results are reliable with the results of XRD as shown in Figure 1a. When the annealing temperature increased from 350 to 550 °C owing to the phase transformation, the grain size also increases as can be seen in the SEM analysis.

The surface area and porosity of the prepared samples were investigated by nitrogen adsorption/desorption and the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) pore size distribution analyses calcined at different temperatures are presented in Figure 2a–f. All samples calcined at different temperatures exhibit a type IV isotherm H4 hysteresis loop, which indicates the mesoporous structure. The pore volume, pore density, and relative pore size distribution vary for all samples. The
structural parameter and BET specific surface area of the synthesized nanoparticles are derived from isotherms and tabulated in Table 1. The pore size distribution in all three different samples ranges between ∼3 and 10 nm. The point of inflection at a relative pressure of ($P/P_0 = 0.4$) represents the monolayer coverage with a mesoporous structure. The obtained values from isotherms reveal that the calcination temperature has a significant impact over the specific surface area of the samples. As the calcination temperature of the sample increases, the specific surface area decreases, which could be due to the agglomeration of particles as can be seen in the SEM analysis. At high temperatures, there is a change in the hysteresis loop, which could be attributed to the widening of the pore size. The high specific surface area and relative pore size distribution provide a better pathway for electrochemical performance.

**Table 1. Surface Area Analysis Results of the Cu$_2$O at 350 and CuO at 450 and 550 °C**

| Sample       | Surface Area (m²/g) | Pore Volume (cc/g) | Pore Diameter (nm) |
|--------------|---------------------|--------------------|--------------------|
| Cu$_2$O 350 °C | 45.312              | 0.086              | 3.407              |
| CuO 450 °C   | 21.910              | 0.025              | 3.408              |
| CuO 550 °C   | 8.182               | 0.020              | 3.819              |

**Figure 3.** SEM images analysis of copper oxides at (a,b) 350 °C, (c,d) 450 °C, and (e,f) 550 °C.
To evaluate the surface morphology and structural features, the prepared samples were examined by SEM spectroscopic techniques as shown in Figure 3a-h. The Cu$_x$O sample obtained in the typical temperature treatment at 350 °C was dominated by many bundles of pithecellulose-type hierarchical matrix with a hollow shape at the center. The porosity and hollow structure were formed due to evolution of CO$_2$ during heat treatment. The magnified SEM image in Figure 3b focuses on some hierarchical individual entity to enlighten the morphology of the samples. Similarly, the SEM of the sample obtained at 450 °C is shown as each pithecellulose-type hierarchical entity is aligned layer by layer and formed a more compact shape than at 350 °C. However, the SEM of the sample obtained at 550 °C shows a columnar stacking of different layers of different shapes, sizes, and dimensions of the particles. Here, the grain size of the particles increases, which may be due to the heating effect on the sample and high degree of agglomeration. The images at high magnification reveal that the particles get agglomerated and form nanoclusters at higher temperatures. From the observed surface morphology of the as-synthesized nanoparticles, it is clear that the porosity as well as the reduced average grain size could provide better morphology/platform for the supercapacitor application. Hence, the pore size and surface morphology at 350 °C (Cu$_x$O) are better than those of CuO. Therefore, the porous structure and small grain size is desirable for use in supercapacitors because they provide ease in the transportation of ions, which leads to delivering of high specific capacitance.

2.2. Electrochemical Study. To evaluate the electrochemical performance of as-synthesized materials (Cu$_2$O and CuO), cyclic voltammetry (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS) were employed. The 1 M KOH aqueous solution, platinum electrode, and Ag/AgCl electrode were used as the electrolyte, counter electrode, and reference electrode respectively. The working electrode was prepared by coating

Figure 4. (a) CV of bare Ni-foam, (b-d) CV of Cu$_2$O and CuO with different temperatures, (e) bar graph of specific capacitance, and (f) linear plot of oxidation peaks.
an adequate amount of sample with Ni-foam. The CV/w of copper oxide nanoparticles at different temperatures were evaluated and compared. The CV of as-synthesized materials is presented in Figure 6b–d within the potential range from 0.1 to 0.6 V with different scan rates (5, 10, 25, 50, 75, and 100 mV/s) respectively. The enclosed surface area and current in case of coated copper oxide are higher than those of the bare Ni-foam as shown in Figure 4a. Figure 4b shows the CV profile demonstrating the anodic and cathodic peaks, indicating that CuO redox reaction occurs during the electrochemical energy storage procedure. The obtained profile reveals that the electrochemical energy storage mechanism is supportive of pseudocapacitance behavior, which is completely different from the EDLC capacitors. The pseudocapacitance behavior of the electrode materials is due to the transition of oxidation state of copper from Cu(I) to Cu(II) and vice versa. During the electrochemical phenomena, the anodic peak of Cu2O seems to be oxidized to Cu(OH)2 and CuO.23,41,42 Similarly, the presence of cathodic peaks are owing to the transformation of the CuO electrode to Cu(OH)2 in Cu2O through the reduction process. The possible reaction between Cu(I) and Cu(II) could be shown by the following equations.

\[
\text{Cu}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{CuO} + \text{H}_2\text{O} + 2e^- \quad (2)
\]

\[
\text{Cu(OH)}_2 + 2e^- \rightarrow 2\text{CuO} + 2\text{H}^+ + \text{H}_2\text{O}^- \quad (3)
\]

In pseudocapacitive materials, the scan rate plays an important role to determine whether the surface specific capacitance arises from bulk diffusion or redox reaction. Almost a linear relationship occurs, suggesting that the diffusion rate was controlled during the electrochemical phenomena.43 Figure 4c,d demonstrated the CV profile of CuO nanoparticles at 450 and 550 °C, respectively. The nature of the CV profile seems to be identical for both cases as discussed earlier. With the change in the scan rates, almost similar CV shapes were observed, indicating the excellent electrochemical performance, high reversibility, and good rate capability of the electrode materials. The improved electrochemical performance in the composite materials might be due to the synergistic effect of both the electrode material and the conducting carbon black. The synergistic effect could be attributed to the alteration of the electronic and structural property of the component present in the system.

For the quantitative measurement, the specific capacitance of the entire prepared sample was calculated by using the following equation.

\[
\text{Specific capacitance (F/g)} = \int \text{IdV}/m \times \text{SR} \times V \quad (4)
\]

where I = current, m = active mass, V = potential, and SR = scan rate (mV/s).

The specific capacitance of CuO@C and CuO@C has been calculated at the scan rate 5 mV/s, observed 1355, 903, and 724 F/g, respectively. It has been found that as the scan rate increases, the specific capacitance value decrease, which suggests that the materials are supercapacitive in nature. When the oxalate sample was annealed to 450 and 550 °C, then the phase transition occurred and CuO was formed. Notably, it seems that the electrochemical performance (specific capacitance of the copper oxide obtained at 450 and 550 °C) is slightly lower than that of Cu2O at 350 °C. This deteriorating electrochemical performance could be due to the high degree of agglomeration, which reduces the active sites for the transference of ions between the electrolyte and electrode materials. The detailed calculated value of the above synthesized materials is listed in Table 2 and is also presented in a bar graph as shown in Figure 4e. The comparative study of various CuO-based electrode materials in a three-electrode system is enlisted in Table 3, showing that the dual-phase Cu2O material developed in the present study has better performance than others. Figure 4f shows the linear graph indicating the direct relationship between current and scan rate. The current produced at different scan rates is taken from the oxidation peaks of each CV. The as-synthesized CuO electrode contains linear dependence and the value of R' in the range of 0.970, 0.986, and 0.968 for copper oxide at 350, 450, and 550 °C, respectively. The obtained results demonstrate that the prepared sample will be treated as one of the suitable electrode materials for energy storage devices in future endeavors.

To further establish the electrochemical properties for the synthesized electrode material, charging–discharging has been evaluated. The galvanostatic charging–discharging profiles of the prepared electrode material at different current densities of 1 to 4 Ag−1 within the potential window 0.1 to 0.6 V in 1 M KOH electrolytic solutions are shown in Figure 5a–c. The nonlinear features of the charging–discharging profile for all three cases are different from the typical triangular shape of EDL Cs, which could be attributed to the pseudocapacitive nature of the prepared electrode material.55 The discharge time of the materials (CuO@C, at 350 °C) was obtained and was longer than that of the bare Ni-foam electrode and CuO@C at 450 and 550 °C, which exhibits all the electroactive sites of copper oxide. The smooth and almost symmetric charging–discharging profile appears in all cases (Figure 5a–c), demonstrating the good pseudocapacitive characteristics indicating the redox reversibility of typical electrode materials. The discharge time profile in case of CuO is larger than that of the CuO nanoparticles, which may be probably the orientation of specific crystal facets which enhance the conductivity due to the small crystallite size and porous nature as seen in the SEM morphology.

Further the electrochemical behavior of the as-synthesized materials was further confirmed from frequency behavior measurement by using EIS as shown in Figure 5d. It is an effective technique to evaluate the interfacial properties of the materials. It is the plot of imaginary part (Z″) versus real part (Z'), signifying about equivalent series resistance.56 From the Nyquist plot, it can be seen that a partial semicircle appears in the high-frequency region corresponding to the electron charge transfer resistance due to the existence of the Faradic redox process at electrode/electrolyte interface whereas a line observed at the low-frequency region could be attributed to the electron transfer diffusion process.57,58 At the low-
frequency region, the lines are perpendicular to the real axis, confirming the ideal supercapacitor, but here the lines are deviated from the ideal one, which can be ascribed to the pseudocapacitance properties of the materials. The diameter of the semicircle measures the charge-transfer resistance ($R_{ct}$), which controls the electrons transfer kinetics at the surface of the electrode. The extent of semicircular arc can be treated as one of the direct and sensitive parameters to depict the interfacial properties of the electrode and electrolyte interface. From the observed data, it can be seen that the materials annealed at 350 °C (Cu$_2$O@C) exhibit the lowest charge-transfer resistance among all electrode materials. Hence, EIS results ensure that materials at 350 °C possess efficient charge transfer as compared to the bare material as well as material annealed at 450 and 550 °C, respectively.

Figure 5e is the Randles circuit for Cu$_2$O nanoparticles, which exhibit a semicircular arc at the high-frequency region and a straight line segment in the low-frequency region, suggesting the capacitive behavior. From the fitted circuit, bulk solution resistance (0.331 Ω) can be calculated from the X
intercept and Faradic charge-transfer resistance (1.074 Ω) can obtained from the semicircular arc in the high-frequency region. The obtained $R_s$ and $R_{ct}$ values confirm the conductivity and facilitate the charge transfer at the electrode/electrolyte interface.

The temperature-dependent Nyquist plot of Cu$_x$O has been evaluated. It is observed in Figure 6a–c that the radius of the Nyquist plots increases with an increase in temperature in each case of copper oxide, which depicts the increase in resistance and consequently decrease in conductivity of the as-synthesized copper oxide nanoparticles. The semicircle arcs represent the grain boundary effects, which involve a parallel combination of grain boundary resistance and capacitance. Besides, the center of each semicircular arc demonstrates a reasonable shift from the real part of impedance Z’, which suggests the occurrence of the non-Debye type of relaxation behavior in Cu$_x$O. The increase of the radius in each semicircle is a further witness of polarization phenomena with a distribution of relaxation time.

3. CONCLUSIONS
In summary, the synthesis of copper oxides (Cu$_2$O and CuO) at three different temperatures was achieved using thermal decomposition of copper oxalate. The temperature-effective formation of the phase from Cu$_2$O (cubic) pithecellobium-type hierarchical dual-phase nanostructured Cu$_x$O to columnar self-assembling of CuO (monoclinic) and its associated behavior were studied systematically by using various physicochemical standard characterization techniques. The electrochemical performances of the prepared copper oxide nanoparticles were examined in a three-electrode assembly cell. The Cu$_2$O system exhibits the maximum specific capacitance performance value of 1355 F/g, whereas in the CuO system (at 450 and 550 °C) it possesses 903 and 724 F/g values at a scan rate of 2 mV/s. The specific capacitance value of Cu$_2$O nanoparticles was higher than that of the CuO nanoparticles, which could be ascribed to the higher surface area and porous morphology. At higher temperatures, the particles get agglomerated, which shorten the diffusion times of the electrolytic ions and electrons, reducing the internal and charge-transfer resistance during the electrochemical process. The current electrode material possesses a significant higher specific capacitance than other reported similar electrode materials in the three-electrode system and has significant potential as a low-cost electrode material for the energy-storage devices.

Figure 6. (a–c) Impedance spectra of Cu$_x$O with different temperatures.
4. EXPERIMENTAL SECTION

4.1. Materials. All the reagents were of analytical grade and used without further any purification. Copper sulfate (CuSO₄·H₂O 99%), ammonium oxalate [(COONH₄)₂, 99%], and ethylene glycol (EG) were purchased from Merck Emplura Pvt. Ltd. (Germany). All the studies were carried out by using distilled water.

4.2. Synthesis of Copper Oxide Nanoparticles. In a typical synthesis process, copper oxides are synthesized from copper oxalate through the calcination route. In general, 0.2 M aqueous copper sulfate was mixed with EG (with different concentrations), which was stirred for 15 min; after that ammonium oxalate (0.2 M) was added and it was further sonicated for another 1 h. The resulting precipitate was filtered off, washed with distilled water several times, and the residue was collected in a Petri dish and kept it in the oven at 60 °C.

4.3. Characterization. Structural and morphological characterization of as-synthesized copper oxide nanoparticles was analyzed by using various physicochemical techniques. FT-IR studies were carried out at room temperature in the range of 400—4000 cm⁻¹ by using KBr pellets in a Nicolet FT-IR Spectrometer. The absorption spectra were recorded by PerkinElmer Lambda-35 UV—visible Spectrophotometer. X-ray powder diffraction patterns were taken in reflection mode with Cu Kα (λ = 1.5406 Å) radiation in the 2θ range from 10 to 80° by using a Seimens D5000 X-ray diffractometer by continuous scanning. The morphologies of the samples were investigated by SEM) by using an FEI (TECNAI G2 20, TWIN) operating at 200 kV, equipped with a GATAN CCD camera. The Raman spectra were taken using a Renishaw plc, Gloucestershire, UK, equipped with a 514 nm green laser having 1 cm⁻¹ spectral resolution of Raman shift, X—Y step resolution of 0.1 μm, and confocal resolution of 2.5 μm.

4.4. Electrochemical Measurements. The electrochemical measurements were carried out using an electrochemical workstation CHI 680 E model. A conventional three-electrode system was used for the electrochemical performance in 1 M KOH electrolytic solution. An Ag/AgCl electrode (saturated KCl) and a Pt electrode were used as the reference and counter electrodes, and Ni-foam was used as the working electrode. The working electrode material was prepared by mixing active material (CuOₓ), carbon black, and polyvinylidene fluoride in 80:10:10 mass ratios mixed with an agate mortar and pestle. To make a homogeneous slurry, 2 mL of 1-methyl-2-pyrrolidone (NMP) was added to the preceding mixture and followed by sonication for 30 min. The working electrode was prepared by adhering the desired amount of sample over the surface Ni-foam (1 cm x 1 cm) by a drop-casting process using the micropipette and allowing to dry at 80 °C for 12 h. CV was carried out within the potential window of 0.1 to 0.6 V at different scan rates, 5, 10, 25, 50, 75, and 100 mVs⁻¹, respectively. EIS was performed in the frequency range 10⁶ to 1 Hz, and the applied amplitude was 0.005 V versus open circuit potential.

■ AUTHOR INFORMATION

Corresponding Author

Mamata Mohapatra — CSIR-Institute of Minerals and Materials Technology, Bhubaneswar 751013, India; Kishor Kumar Sahu — CSIR-Institute of Minerals and Materials Technology, Bhubaneswar 751013, India; Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, Uttar Pradesh 201 002, India; Benjamin Raj — CSIR-Institute of Minerals and Materials Technology, Bhubaneswar 751013, India; Suddhasatwa Basu — CSIR-Institute of Minerals and Materials Technology, Bhubaneswar 751013, India; Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, Uttar Pradesh 201 002, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03899

Notes

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