Fabrication of Bimetallic Oxides (MCo$_2$O$_4$: M=Cu, Mn) on Ordered Microchannel Electro-Conductive Plate for High-Performance Hybrid Supercapacitors

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Abstract: AB$_2$O$_4$-type binary-transition metal oxides (BTMOs) of CuCo$_2$O$_4$ and MnCo$_2$O$_4$ were successfully prepared on ordered macroporous electrode plates (OMEP) for supercapacitors. Under the current density of 5 mA cm$^{-2}$, the CuCo$_2$O$_4$/OMEP electrode achieved a specific capacitance of 1199 F g$^{-1}$. The asymmetric supercapacitor device prepared using CuCo$_2$O$_4$/OMEP as the positive electrode and carbon-based materials as the negative electrode (CuCo$_2$O$_4$/OMEP//AC) achieved the power density of 14.58 kW kg$^{-1}$ under the energy density of 11.7 Wh kg$^{-1}$. After 10,000 GCD cycles, the loss capacitance of CuCo$_2$O$_4$//OMEP//AC is only 7.5% (the retention is 92.5%). The MnCo$_2$O$_4$/OMEP electrode shows the specific and area capacitance of 843 F g$^{-1}$ and 5.39 F cm$^{-2}$ at 5 mA cm$^{-2}$. The MnCo$_2$O$_4$/OMEP-based supercapacitor device (MnCo$_2$O$_4$/OMEP//AC) has a power density of 8.33 kW kg$^{-1}$ under the energy density of 11.6 Wh kg$^{-1}$ and the cycle stability was 90.2% after 10,000 cycles. The excellent power density and cycle stability prove that the prepared hybrid supercapacitor fabricated under silicon process has a good prospect as the power buffer device for solar cells.

Keywords: power buffer; silicon micromachining; bimetallic oxide; ordered macropore structure; electrochemical; supercapacitor

1. Introduction

Currently, with the continuous expansion of energy demand, as an important device to stabilize energy input and output, the research on energy storage components has become more and more the focus of future sustainable development [1]. After the solar cell generates electric energy, storing this energy through the energy storage system integrated with microelectronic technology to fulfill the stable and safe utilization of energy remains a challenge for the efficient application of solar energy [2,3]. The complex environment of solar cell power generation and storage is pursuing the characteristics of high-power density, long lifecycle and low cost, which are consistent with the research concept of electrode materials for supercapacitors [4]. Binary transition metal oxides (BTMOS) are
important multifunctional materials composed of two metal elements. Due to their unique structure and properties, they have attracted extensive attention in catalysis, heavy metal ion adsorption, electrocatalyst, sensor, lithium-ion batteries and supercapacitors [5–8]. Among those bimetallic oxides, cobalt-based AB2O4 BTMOS such as CuCo2O4, ZnCo2O4, NiCo2O4, MnCo2O4 and FeCo2O4 have attracted extensive attention due to their high specific capacitance, better rate performance and stability electrochemical properties, and are considered to have the most potential electrode material for energy storage, especially supercapacitors [9–13].

Cu, Mn, Fe and other metal atoms replace Co atoms in Co3O4 to form a MCo2O4 type bimetallic oxide, which increases the Faraday redox reaction site with a higher capacity and reduces the production cost of the active material without changing the spinel structure of Co3O4 [11,14,15]. However, the untreated bimetallic oxides have low conductivity and are easy to agglomerate during the reaction, which limits their further application in supercapacitors [16,17]. Selecting appropriate bimetallic oxides, and then advanced electrode structure design and nanomaterial preparation process, is an effective means to enhance the ion transport and structural stability of bimetallic oxides in the process of electrochemical reaction. Among those MCo2O4 type materials, CuCo2O4 and MnCo2O4 are two kinds of active materials with different electrical active elements, which have received extensive attention in recent years [16,18–20]. Zhang et al. [21] reported the specific capacitance of CuCo2O4@Cu2O/MnO2//Ni foam electrode up to 888.9 F g−1 at 2 mA cm−2; Pang et al. worked on δ-MnO2-added CuCo2O4 which shows a maximum specific capacitance of 1180 F g−1 at 1 A g−1 and remains 93.2% after 5000 GCD cycles [22]. Lee’s MnCo2O4-NiCo2O4 composite electrodes exhibit a high specific capacitance of 1152 F g−1 at 1 A g−1, and excellent rate capability and superior cycling stability (95.38% retention after 3000 cycles) [23]. These studies showed that the cobalt-based bimetallic oxide has a good application prospect for energy storage equipment.

Here, MCo2O4 (M=Cu, Mn) nanosheets were prepared on a three-dimensional ordered macroporous electrode plate (OMEP) through the hydrothermal method as high-performance multi-dimensional Faraday electrodes [24]. Although there are many studies on porous materials in the field of energy storage in recent years, there is little similar research on ordered porous materials such as OMEP, and the research materials combined with AB2O4 bimetallic oxides have just emerged [21]. OMEP, composed of millions of neatly arranged porous structures fabricated by the silicon micromachining process, acts as a conductive substrate in the multidimensional composite electrode to effectively prevent the agglomeration of nanomaterials [25,26]. A stable nickel coating on the OMEP surface not only can improve the electrical conductivity of the electrode, but it also acts as the nucleation center of the active material, allowing the active material to adhere tightly to the surface of the nickel layer, without the need for an additional conductive agent or polymer binder. Therefore, the electrodes prepared with OMEP can objectively reflect the performance characteristics of specific active substances.

In this paper, CuCo2O4/OMEP electrodes and MnCo2O4/OMEP electrodes were successfully prepared by using nickel-plated ordered macroporous electrode-conductive plates (OMEP) as the substrate. These composite electrodes have a unique three-dimensional porous structure, which facilitates the transport of electrons and ions, increases the liquid-solid interface area, improves the utilization efficiency of the active material and reduces the weight and size of the electrode, which makes the active material obtain a large specific capacitance for miniature supercapacitors [27]. The MnCo2O4/OMEP electrode shows the specific and area capacitance of 843 F g−1 and 2.7 F cm−2 at 5 mA cm−2. The MnCo2O4/OMEP-based supercapacitor device (MnCo2O4/OMEP//AC) has a power density of 8.33 kW kg−1 under the energy density of 11.6 Wh kg−1 and the cycle stability was 90.2% after 10,000 cycles. The CuCo2O4/OMEP electrode has high cycle stability and maintains a good ratio at a higher current density and CV scanning speed. The specific capacitance of the electrode is 1199 F g−1 at the current density of 5 mA cm−2. The asymmetric supercapacitors prepared using the CuCo2O4/OMEP electrode and activated carbon
electrode (CuCo$_2$O$_4$/OMEP//AC) has obtained the power density of 14.58 kW kg$^{-1}$ under the energy density of 11.7 Wh kg$^{-1}$. After 10,000 GCD cycles, the loss capacitance of CuCo$_2$O$_4$/OMEP//AC is only 7.5%.

2. Materials and Methods

2.1. Preparation of OMEP

The silicon macroporous microchannel plate (Si-MCP, Figure 1a,b) is the skeleton structure of OMEP. Its fabrication process can be divided into three steps: pretreatment, deep etching and stripping. Pretreatment stage: select (100) crystal p-type silicon wafer, grow silica mask layer through thermal oxidation, define the hole pattern by lithography, use buffered oxide etchant (BOE) etching solution to expose the holes that need to be etched from the silica mask layer, remove the photoresist to obtain the desired pattern. The wafer is anisotropically etched in 25% tetramethylammonium hydroxide solution and stops etching when a distinct cross pattern is seen under the microscope. The pretreated silicon wafer was subjected to deep photochemical etching [28] and the peel steps are followed to obtain the required Si-MCP. A layer of nickel was uniformly deposited on the outer and inner surfaces of Si-MCP by liquid flow method [29–31] to fabricate the OMEP (Figure 1c–f). To further improve the electrical conductivity and specific surface area of the OMEP, the electroplating nickel method was carried out to deposition a nickel particle layer on OMEP after chemical deposition. At room temperature of (23 ± 1)°C, the electrolyte consisted of 2 M ammonium chloride and 0.1 M nickel chloride, and the pH was adjusted to 3.5. After nickel deposition, the morphologies of the surface and sidewalls at different magnification are shown in Figure 1c–f. It can be seen from the figure that a layer of nickel evenly covers the surface and sidewalls of the Si-MCP.

2.2. Synthesis of the CuCo$_2$O$_4$/OMEP and MnCo$_2$O$_4$/OMEP Electrode

To fabricate the CuCo$_2$O$_4$/OMEP electrode, a mixture of 1 mmol copper nitrate and 2 mmol cobalt nitrate was added with 15 mmol urea as precipitators. The solution was fully stirred and mixed and put into a reactor with OMEP in front of it. The hydrothermal reaction lasted for 8 h at 120 °C and then cooled to room temperature naturally. The CuCo$_2$O$_4$/OMEP electrode was prepared after the samples were rinsed and dried at 60 °C.

Figure 1. SEM images: (a) top surface of the ordered Si-MCP; (b) sidewall of Si-MCPs; (c,d) top surface of nano-Ni covered OMEP with different magnification; (e,f) sidewall of OMEP with different magnification.
for 24 h. The preparation method and steps of the MnCo$_2$O$_4$/OMEP electrode are the same as the CuCo$_2$O$_4$/OMEP electrode, but the difference is that the copper nitrate used in CuCo$_2$O$_4$/OMEP fabrication is replaced by manganese sulfate in hydrothermal reaction. The procedure for preparing samples on the surface of nickel foam is consistent with that of OMEP-based samples, except that the substrate is changed from OMEP to nickel foam. At the same time, the CuCo$_2$O$_4$ and MnCo$_2$O$_4$ fabricated on nickel foam were named CuCo$_2$O$_4$/NF and MnCo$_2$O$_4$/NF, respectively.

2.3. Characterization

Scanning electron microscopy (SEM, JEOLJSM-7001F, Tokyo, Japan) was used to study the morphology and microstructure of various electrodes. X-ray diffraction (XRD, Rigaku, RINT2000, Tokyo, Japan) was used to study the crystal structure and X-ray photoelectron spectroscopy (XPS, Kratoms Axis Ultra DLD) was used to determine the elemental composition of the fabricated electrodes.

In this paper, CHI660E electrochemical workstation was used to perform performance tests in 2 M KOH electrolyte. OMEP, Co$_3$O$_4$/OMEP, CuCo$_2$O$_4$/NF, MnCo$_2$O$_4$/NF, CuCo$_2$O$_4$/OMEP and MnCo$_2$O$_4$/OMEP electrodes were used as the working electrodes, saturated calomel electrode as the reference electrode and platinum wire electrode as the counter electrode. The electrochemical properties of the composite electrodes were characterized by cyclic voltammetry (CV), charge-discharge analysis (GCD) and electrochemical impedance spectroscopy (EIS).

3. Results

3.1. Material Properties

3.1.1. Electrodes SEM Morphology Analysis

As shown in Figure 1a,b, the Si-MCP composed of millions of neatly arranged porous structures acts as the foundation for making OMEP that compatible with the microelectronics process. After the two-step nickel deposition methods on Si-MCPs, the OMEP (Figure 1c–f) was fabricated with rough morphology and excellent conductivity. SEM images of the CuCo$_2$O$_4$/OMEP electrode and the MnCo$_2$O$_4$/OMEP electrode are shown in Figures 2 and 3, respectively. The nickel layer deposit on OMEP can make the active material closely adhere to the electrode plate as the nucleation center of CuCo$_2$O$_4$ and MnCo$_2$O$_4$ nanosheets. Figure 2 shows the images of CuCo$_2$O$_4$/OMEP (Figure 2a–d) electrode. The nanoscale CuCo$_2$O$_4$ is uniformly deposited on the surface of OMEP, and the micropores of OMEP are retained, which is conducive to the transport of electrolytes inside the electrode. Figure 2e,f shows the sidewall of the CuCo$_2$O$_4$/OMEP electrode with different magnification, and the morphologies of the CuCo$_2$O$_4$ nanosheets in the cross-section are not the same as the nanosheets on the surface, which may be caused by different solution contact environments in the high aspect ratio channel during the hydrothermal reaction. According to the elemental analysis of the CuCo$_2$O$_4$/OMEP electrode from Figure S1a, it is found that the atomic percentage of Ni is 59%. The ratio of Cu, Co and O atoms was close to 1:2:4, which were 6%, 13% and 22%, respectively.

Figure 3 shows the SEM image of MnCo$_2$O$_4$/OMEP composite electrode. According to the SEM image in Figure 2a–c, it can be found that MnCo$_2$O$_4$ nanosheets are denser than CuCo$_2$O$_4$ nanosheets, and these morphological and structural characteristics may cause the loss of specific capacity of MnCo$_2$O$_4$. On the other hand, because MnCo$_2$O$_4$ is more compact, there are more active materials per unit area on the MnCo$_2$O$_4$/OMEP electrode that achieve a larger surface capacitance than that of CuCo$_2$O$_4$/OMEP. However, the loose distribution of CuCo$_2$O$_4$ nanosheets can reduce the loss of capacitance under high CV scanning speed and large current density. Figure S1b shows the SEM mapping of the CuCo$_2$O$_4$/OMEP electrode, from which the atomic percentage of Ni is 39%. Cu, Co and O atoms accounted for 9%, 18% and 34%, respectively. To make a comprehensive analysis of the performance of OMEP as the supercapacitor substrates, the electrodes based on nickel foam were also prepared and characterized under the same conditions. Figures S2 and S3
show the SEM images of CuCo$_2$O$_4$ and MnCo$_2$O$_4$ deposited on the surface of nickel foam, respectively. From these diagrams, it can be seen that the nanomaterials formed on nickel foam are nanowires, which are completely different from those deposited on the OMEP surface, although their preparation conditions are identical. The above observation and analysis show that the unique substrate structure and surface characteristics can control the morphology of the prepared nanomaterials, and further affect the electrochemical performance of the electrodes.

**Figure 2.** SEM images: (a–d) top surface of CuCo$_2$O$_4$/OMEP with different magnification; (e,f) side wall of CuCo$_2$O$_4$/OMEP with different magnification.

**Figure 3.** SEM images: (a–d) top surface of MnCo$_2$O$_4$/OMEP with different magnification; (e,f) sidewall of MnCo$_2$O$_4$/OMEP with different magnification.
### 3.1.2. Electrode Structure and Composition Analysis

The structures of OMEP and nanocomposite electrodes were determined by X-ray diffraction, as shown in Figure 4a. The XRD pattern of CuCo$_2$O$_4$/OMEP and MnCo$_2$O$_4$/OMEP has the strong peak of active materials of CuCo$_2$O$_4$ and MnCo$_2$O$_4$, respectively. The diffraction peaks of backbone substrate of OMEP only have stronger Ni (JCPDS Card No. 01-089-7128) and Si peaks, indicating that the active materials were successfully deposited on the substrate. By comparing the No. 001-1155 card in JCPDS, it can be verified that the composite electrode is successfully attached with the CuCo$_2$O$_4$ material, and the CuCo$_2$O$_4$/OMEP composite electrode matches the peaks of the crystal faces (311), (422) and (440) on the No. 78-2177 card in JCPDS of CuCo$_2$O$_4$. The crystal face of CuCo$_2$O$_4$ is the highest peak at (311), indicating that the CuCo$_2$O$_4$ nanosheets grow preferentially along the direction of (311) [20]. In addition, a dense CuCo$_2$O$_4$ nanosheet with a thickness of about 300 nm is covered on the surface of OMEP, which weakens the peak strength of Ni (red line). The pink line is the XRD pattern of the MnCo$_2$O$_4$/OMEP electrode. By comparing the No.023-1237 card in JCPDS, the XRD pattern of MnCo$_2$O$_4$/OMEP composite electrode matches the peaks of the crystal faces (220), (222), (400) and (422) on the card. The other spikes occur due to the influence of OMEP plates.

![Figure 4.](image)

**Figure 4.** (a) XRD patterns of CuCo$_2$O$_4$/OMEP, MnCo$_2$O$_4$/OMEP and OMEP; (b) XPS survey spectrum of CuCo$_2$O$_4$/OMEP and MnCo$_2$O$_4$/OMEP; XPS spectra of (c) Cu 2p and (d) Co 2p for CuCo$_2$O$_4$/OMEP; XPS spectra of (e) Mn 2p and (f) Co 2p for MnCo$_2$O$_4$/OMEP.

Figure S4 and Figure 4b–f provide the XPS general patterns and interval diagrams of the CuCo$_2$O$_4$/OMEP electrode and the MnCo$_2$O$_4$/OMEP electrode, respectively. By observing Figure 4b, it is found that the peak position of C 1s appears at 285 eV, which is consistent with the XPS standard energy spectrum. In Figure S4, O 1s peaks are subdivided into metal–oxygen bonds (M-O, M: Co, Cu and Mn) and oxygen-containing groups (H-O) [32]. XPS images show that the adsorption of oxygen and hydroxyl groups in CuCo$_2$O$_4$ and MnCo$_2$O$_4$ crystal on the surface of the nanostructure are the two main factors affecting the nanostructure [33]. Compared the Figure S4a,b, it can be found that the O 1s peak of the MnCo$_2$O$_4$/OMEP electrode is shifted to the right, which may be caused by the more abundant valence states of Mn. Figure 4c shows the interval XPS map of Cu 2p. The peak of Cu 2p$_{3/2}$ appears at 936 eV, and the peak of Cu 2p$_{1/2}$ at 956 eV. Cu$^{2+}$ and Cu$^{+}$ constitute...
the main valence states of Cu 2p [19,34]. The corresponding Figure 4e shows the Mn 2p pattern of the MnCo$_2$O$_4$/OMEP electrode. The peak of Mn 2P$_{3/2}$ appears at 643 eV, and the peak of Co 2P$_{1/2}$ at 655 eV. Mn$^{2+}$ and Mn$^{3+}$ are the main valence states of Mn 2p [35,36]. Figure 4d,f show that Cu and Mn do not affect the spectral arrangement of Co 2p. The peak of Co 2P$_{3/2}$ appears at 782 eV, the peak of Co 2P$_{1/2}$ at 798 eV and the satellite peaks (Sat.) of Co 2P$_{3/2}$ and Co 2P$_{1/2}$ appear at 787 eV and 803 eV, respectively. Among them, Co$^{3+}$ and Co$^{2+}$ are the main valence states of Co 2p [37].

3.1.3. Electrodes Electrochemical Performance Analysis

The redox reaction principle of CuCo$_2$O$_4$ and MnCo$_2$O$_4$ nanomaterials in alkaline solution as follows [38,39]:

\[
\begin{align*}
\text{CuCo}_2\text{O}_4 + \text{H}_2\text{O} + \text{e}^- &\rightleftharpoons 2\text{CoOOH} + \text{CuOH} \\
\text{CuOH} + \text{OH}^- &\rightleftharpoons \text{Cu(OH)}_2 + \text{e}^- \\
\text{MnCo}_2\text{O}_4 + \text{H}_2\text{O} + \text{OH}^- &\rightleftharpoons 2\text{CoOOH} + \text{MnOOH} \\
\text{MnOOH} + \text{OH}^- &\rightleftharpoons \text{MnO}_2 + \text{H}_2\text{O} + \text{e}^- \\
\text{CoOOH} + \text{OH}^- &\rightleftharpoons \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^- 
\end{align*}
\]

Figure 5 illustrates the CV and GCD results of electrodes based on CuCo$_2$O$_4$ and MnCo$_2$O$_4$. Figure 5a shows that CuCo$_2$O$_4$/OMEP and MnCo$_2$O$_4$/OMEP have a much better capacitance than CuCo$_2$O$_4$ and MnCo$_2$O$_4$ prepared on nickel foam. Correspondingly, the sample based on OMEP has a larger CV disclose area (Figure 5a, 10 mV s$^{-1}$ scan rate) and longer discharge time (Figure 5b, 5 mA cm$^{-2}$ current density). As shown in Figure 5c, the CV curve of the CuCo$_2$O$_4$/OMEP electrode presents a rectangle, and the CV curve gradually increases with the increase in scanning speed. Figure 5d depicts the GCD curve of the CuCo$_2$O$_4$/OMEP electrode. In the discharge process, the voltage and current of the CuCo$_2$O$_4$/OMEP electrode are linear.

![Figure 5](image-url)

**Figure 5.** (a) Cyclic voltammetry curves at the scanning rate of 10 mV S$^{-1}$ and (b) 5 mA cm$^{-2}$ charging–discharging curves of the newly fabricated CuCo$_2$O$_4$/NF, MnCo$_2$O$_4$/NF, CuCo$_2$O$_4$/OMEP and MnCo$_2$O$_4$/OMEP electrode; CuCo$_2$O$_4$/OMEP (c) CV curves at different scanning rates and (d) charging–discharging curves at different current densities; MnCo$_2$O$_4$/OMEP (e) CV curves at different scanning rates and (f) charging–discharging curves at different current densities.
In Figure 5e, the redox peak of the MnCo$_2$O$_4$/OMEP electrode is obvious. When the scanning speed exceeds 15 mV s$^{-1}$, obvious deformation occurs in the closed region of the CV curve of the MnCo$_2$O$_4$/OMEP electrode. Figure 5f shows the GCD curve of the MnCo$_2$O$_4$/OMEP electrode, indicating that the specific capacitance of this electrode is mainly contributed by the double layer capacitance [40]. Figures S5 and S6 reflect electrochemical chemistry performance of CuCo$_2$O$_4$/NF and MnCo$_2$O$_4$/NF at different CV scanning rates and different current densities after activation. It can be seen from these two pictures that the CV curve and GCD curve of electrodes prepared by the same process on nickel foam are quite different from those based on OMEP. The peaks of the CV curve based on foamed nickel are more obvious, while the OMEP-based electrode curve is more similar to a rectangle, which reflects that OMEP-based samples have more pseudo capacitance components.

To further analyze the positive influence of the fabrication nanomaterials on OMEP and preparation of bimetallic oxides on the performance of supercapacitors, systematic electrochemical tests were also carried out on OMEP and Co$_3$O$_4$/OMEP. Unlike the CV from CuCo$_2$O$_4$/OMEP and MnCo$_2$O$_4$/OMEP, as shown in Figure 6a, the CV from Co$_3$O$_4$/OMEP has a clear redox peak, while CuCo$_2$O$_4$/OMEP and MnCo$_2$O$_4$/OMEP are more likely to be a surface electrochemical pseudocapacitive reaction at high scanning rates. Figure 6b indicates that Co$_3$O$_4$/OMEP has a low specific capacity and surface capacitance because it has fewer active sites and lower conductivity. Figure 6c compares CV curves of OMEP, Co$_3$O$_4$/OMEP, CuCo$_2$O$_4$/OMEP and MnCo$_2$O$_4$/OMEP at different scanning speeds. The results show that the CV area of the CuCo$_2$O$_4$/OMEP electrode is slightly smaller than that of the MnCo$_2$O$_4$/OMEP electrode at low scanning speed (Figure 5a, 5 mV s$^{-1}$). At the same time, the compact structure of MnCo$_2$O$_4$ nanosheets showed a larger surface capacitance. At high scanning speed (Figure 6c, 60 mV s$^{-1}$), the CV area of the CuCo$_2$O$_4$/OMEP electrode is about twice that of the MnCo$_2$O$_4$/OMEP electrode. The reverse overrun of the CV area is attributed to the higher conductivity of CuCo$_2$O$_4$ nanosheets than that of MnCo$_2$O$_4$ nanosheets, and the CuCo$_2$O$_4$/OMEP composite structure is more suitable for a high CV scanning speed environment. Figure 6c discloses that the capacitance of CuCo$_2$O$_4$/OMEP and MnCo$_2$O$_4$/OMEP shows considerably larger capacitance than OMEP and Co$_3$O$_4$/OMEP because of the larger enclosed area in the CV curve and longer discharge time (Figure S7, 5 mA cm$^{-2}$ charging–discharging current).

The specific capacitance of the electrode $C_s$ and the surface capacitance of the CV curve $C_{CV}$ can be calculated according to Equations (6) and (7), and the energy ($E$) and the power ($P$) density were determined according to the equations as follows [41]:

$$C_s = \frac{I \times \Delta t}{m \times \Delta V}$$  \hspace{1cm} (6)

$$C_{CV} = \int idV/(2v \times m \times \Delta V)$$  \hspace{1cm} (7)

$$E = \frac{C \times (\Delta V)^2}{2 \times 3.6}$$  \hspace{1cm} (8)

$$P = \frac{E \times 3.6}{\Delta t}$$  \hspace{1cm} (9)

where $C_s$ (F/g) is the specific capacitance, $I$ (A) is the current density of charge and discharge, $\Delta t$(s) is the discharge time, $m$(g) is the mass of the active substance in the electrode and $\Delta V$(V) is the pressure drop in the test. $v$ (V/s) is the scanning speed of the CV curve. $idV$ is the closed area of the CV curve.

According to Figure 5d, Figure 6d and Equation (6), the specific capacitances of the CuCo$_2$O$_4$/OMEP electrode are 1199 F g$^{-1}$ (5 mA cm$^{-2}$), 1111 F g$^{-1}$ (10 mA cm$^{-2}$), 970 F g$^{-1}$ (15 mA cm$^{-2}$), 928 F g$^{-1}$ (20 mA cm$^{-2}$) and 844 F g$^{-1}$ (25 mA cm$^{-2}$). According to Equation (7), the surface capacitances of the corresponding GCD curve can be further calculated as follows: 4.76 F cm$^{-2}$ (5 mA cm$^{-2}$), 4.40 F cm$^{-2}$ (10 mA cm$^{-2}$), 3.85 F cm$^{-2}$
It can be found that the surface capacitance of the CuCo$_2$O$_4$/OMEP electrode maintains good magnification characteristics, and the surface capacitance is stable at about 2 F cm$^{-2}$ at each scanning speed. According to Figure 6d and Equations (6) and (7), the specific capacitances of the MnCo$_2$O$_4$/OMEP electrode are 843 F g$^{-1}$ (5 mA cm$^{-2}$), 728 F g$^{-1}$ (10 mA cm$^{-2}$), 648 F g$^{-1}$ (15 mA cm$^{-2}$), 564 F g$^{-1}$ (20 mA cm$^{-2}$) and 520 F g$^{-1}$ (25 mA cm$^{-2}$). The surface capacitances corresponding to GCD curves are 5.39 F cm$^{-2}$ (5 mA cm$^{-2}$), 4.60 F cm$^{-2}$ (10 mA cm$^{-2}$), 4.27 F cm$^{-2}$ (15 mA cm$^{-2}$), 3.71 F cm$^{-2}$ (20 mA cm$^{-2}$) and 3.25 F cm$^{-2}$ (25 mA cm$^{-2}$). The results show that with the increase in scanning rate and current density, the surface capacity of the MnCo$_2$O$_4$/OMEP electrode decreases sharply. The specific capacity and surface capacitance of the electrodes mentioned in this paper are shown in Table 1.

It is obvious that due to the compactness of MnCo$_2$O$_4$ nanosheets fabricated on OMEP, the mass of MnCo$_2$O$_4$ per unit area is larger CuCo$_2$O$_4$ on OMEP, so the calculated specific capacity of MnCo$_2$O$_4$/OMEP is lower than that of CuCo$_2$O$_4$/OMEP. In addition, the area capacitance of the MnCo$_2$O$_4$/OMEP electrode is larger than that of the CuCo$_2$O$_4$/OMEP electrode at a lower current density (lower than 15 mA cm$^{-2}$). However, the capacitance of the CuCo$_2$O$_4$/OMEP electrode exceeds that of the MnCo$_2$O$_4$/OMEP electrode in

| Current Density (mA cm$^{-2}$) | CuCo$_2$O$_4$/OMEP (F g$^{-1}$/F cm$^{-2}$) | MnCo$_2$O$_4$/OMEP (F g$^{-1}$/F cm$^{-2}$) | CuCo$_2$O$_4$/NF (F g$^{-1}$/F cm$^{-2}$) | MnCo$_2$O$_4$/NF (F g$^{-1}$/F cm$^{-2}$) | Co$_3$O$_4$/OMEP (F g$^{-1}$/F cm$^{-2}$) |
|-------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| 5                             | 1199/4.76                     | 843/5.39                       | 322/0.77                       | 249/1.05                       | 263/2.10                       |
| 10                            | 1111/4.40                     | 728/4.60                       | 259/0.62                       | 225/0.95                       | 226/1.81                       |
| 15                            | 970/3.85                      | 648/4.27                       | 217/0.52                       | 176/0.74                       | 163/1.30                       |
| 20                            | 928/3.82                      | 564/3.71                       | 185/0.44                       | 130/0.55                       | 113/0.90                       |
| 25                            | 844/3.49                      | 520/3.25                       | 150/0.36                       | 110/0.46                       | 74/0.59                       |
20 mA cm$^{-2}$ and 25 mA cm$^{-2}$ charge and discharge tests. The reason for these phenomena is that the arrangement of MnCo$_2$O$_4$ nanosheets is too dense, so the MnCo$_2$O$_4$/OMEP electrode cannot fully contact the electrolyte at a high charge-discharge speed, resulting in the deformation of the CV curve and the loss of electrical capacity.

Figure 6e shows the EIS pattern of the composite electrode before and after the cycle. It can be observed that the Nyquist curve of the composite electrode consists of an arc in the high-frequency region and an oblique line in the low-frequency region. Among them, the CuCo$_2$O$_4$/OMEP electrode (red line) before the cycle has the shortest arc radius and the highest slope of the inclined line in the low-frequency region, which means that the composite electrode has the lowest impedance and the higher conductivity of the CuCo$_2$O$_4$/OMEP electrode. In addition, the arc radius (red, green line) in the high-frequency region of the composite electrode before the cycle is smaller than the arc radius (orange, blue line) after the cycle, and the slope of the arc in the low-frequency region is higher than the slope of the arc after the cycle. It shows that after 10,000 cycles, the electrical conductivity of the electrode is lost to varying degrees. It can be seen from the intersection of the Nyquist curve and ordinate zero axis that the solution resistance ($R_s$) of CuCo$_2$O$_4$/OMEP electrode and the MnCo$_2$O$_4}$/OMEP electrode before circulation are 2.01 and 2.42 ohms, respectively. After 10,000 cycles, the solution resistance of the CuCo$_2$O$_4$/OMEP electrode was reduced to 1.88 ohms, while the solution resistance of the MnCo$_2$O$_4$/OMEP electrode was increased to 2.68 ohms.

Figure 6f shows 10,000 cycle stability tests for CuCo$_2$O$_4$/OMEP electrodes and MnCo$_2$O$_4$/OMEP electrodes. The measured specific capacitances of the CuCo$_2$O$_4$/OMEP electrode and the MnCo$_2$O$_4$/OMEP electrode at the current density of 5 mA cm$^{-2}$ before the cycle is 1199 F g$^{-1}$ and 843 F g$^{-1}$, respectively. After 10,000 cycles, the specific capacitance of the CuCo$_2$O$_4$/OMEP electrode at the current density of 5 mA cm$^{-2}$ is 1081 F g$^{-1}$, resulting in a 9.8% capacitance loss, while the specific capacitance retention of the MnCo$_2$O$_4$/OMEP electrode in the same condition is 83.5%. The above data indicate that the CuCo$_2$O$_4$/OMEP electrode is more stable than the MnCo$_2$O$_4$/OMEP electrode in terms of cycle stability. This may be due to the introduction of Cu$^{2+}$ and the special structure of CuCo$_2$O$_4$/OMEP, which make it difficult to dissolve and agglomerate in the electrolyte.

3.1.4. Electrochemical Performance Analysis of Hybrid Supercapacitor

CuCo$_2$O$_4$ and MnCo$_2$O$_4$ hybrid supercapacitor devices are prepared by using the MCo$_2$O$_4$/OMEP (M=Cu, Mn) as the positive electrode and carbon-based nickel foam as the negative electrode. The electrochemical properties of the two devices are shown in Figure 7. Figure 7a,c shows that the CV curve closing area of MnCo$_2$O$_4$/OMEP//AC is larger than that of CuCo$_2$O$_4$/OMEP//AC. This is because the active material mass in CuCo$_2$O$_4$/OMEP//AC is 2.4 mg, far less than that in MnCo$_2$O$_4$/OMEP//AC (4.2 mg). More active material provides higher CV surface capacitance of the supercapacitor. According to Figure 7b and Equations (8) and (9), the power density (energy density) of MnCo$_2$O$_4$/OMEP//AC can be calculated as follows: 2.92 KW kg$^{-1}$ (41.7 Wh kg$^{-1}$), 5.83 KW kg$^{-1}$ (30.6 Wh kg$^{-1}$), 8.75 KW kg$^{-1}$ (21.1 Wh kg$^{-1}$), 11.67 KW kg$^{-1}$ (15.2 Wh kg$^{-1}$) and 14.58 KW kg$^{-1}$ (11.7 Wh kg$^{-1}$). Figure 7d shows the charge–discharge curve of MnCo$_2$O$_4$ supercapacitor, and the power density (energy density) can be obtained as follows: 1.67 KW kg$^{-1}$ (25.9 Wh kg$^{-1}$), 3.33 KW kg$^{-1}$ (20.2 Wh kg$^{-1}$), 5.00 KW kg$^{-1}$ (16.8 Wh kg$^{-1}$), 6.67 KW kg$^{-1}$ (14.6 Wh kg$^{-1}$) and 8.33 KW kg$^{-1}$ (11.6 Wh kg$^{-1}$). The comparison of the power and energy density of the two supercapacitors is shown in Figure 7e. In addition, the cyclic stability test results of the supercapacitor are shown in the lower-left corner of Figure 7e. The test showed that after 10,000 cycles, the CuCo$_2$O$_4$ supercapacitor maintained a specific capacitance of 92.5%, while the MnCo$_2$O$_4$ supercapacitor maintained 90.2% capacitance.
4. Conclusions

AB₂O₄-type binary-transition metal oxides (BTMOs) of CuCo₂O₄ and MnCo₂O₄ were successfully prepared on ordered macroporous electrode plates (OMEP) that are compatible with silicon micro-nano processes for supercapacitors. These composite porous electrodes have a unique three-dimensional structure, which facilitates the transport of electrons and ions increases the liquid–solid interface area, improves the active material utilization efficiency and reduces the weight and size of the electrode, which allows the active material to obtain a large specific capacitance. The CuCo₂O₄/OMEP has a capacitance of 1199 F g⁻¹ at the current density of 5 mA cm⁻² and 844 F g⁻¹ at the current density of 5 mA cm⁻². After 10,000 cycles, the capacitance stability achieved 92.5%. The asymmetric supercapacitor device of CuCo₂O₄/OMEP//AC achieves a power density of 14.58 kW kg⁻¹ at the energy density of 11.7 Wh kg⁻¹. The MnCo₂O₄/OMEP electrode
shows a better area capacitance at a small current density (5.76 F cm⁻² at 5 mA cm⁻²) because its compact structure can load more active substances per unit area. The MnCo₂O₄ supercapacitor’s power density is 8.33 kW kg⁻¹ with an energy density of 11.6 Wh kg⁻¹ and its cycle stability was 90.2%, maintained after 10,000 cycles.

### Supplementary Materials
The following are available online at https://www.mdpi.com/article/10.3390/su13179896/s1. Figure S1: SEM mappings of (a) the CuCo₂O₄/OMEP electrode; (b) the MnCo₂O₄/OMEP electrode. Figure S2: SEM images: (a–d) CuCo₂O₄ nanostructures fabricated on nickel foam with different magnification, Figure S3: SEM images: (a–d) MnCo₂O₄ nanostructures fabricated on nickel foam with different magnification, Figure S4: XRD patterns of O s1 for (a) CuCo₂O₄/OMEP and (b) MnCo₂O₄/OMEP. Figure S5: (a) CV curves of CuCo₂O₄/NF at different scanning rates and (b) charging–discharging curves of CuCo₂O₄/NF at different current densities after activation, Figure S6: (a) CV curves of MnCo₂O₄/NF at different scanning rates and (b) charging–discharging curves of MnCo₂O₄/NF at different current densities after activation, Figure S7: charge–discharge curves of the newly fabricated OMEP, Co₃O₄/NF, CuCo₂O₄/OMEP and MnCo₂O₄/OMEP electrode at a current density of 5 mA cm⁻².

### Author Contributions
Conceptualization, M.L. and L.W.; methodology, M.L.; validation, M.L., R.F. and K.Z.; formal analysis, C.W. and J.W.; data curation, M.L., R.F. and F.Z.; writing—original draft preparation, M.L. and R.F.; writing—review and editing, M.L., Z.M. and P.K.C.; funding acquisition, M.L., Z.M. and P.K.C. All authors have read and agreed to the published version of the manuscript.

### Funding
This research was financially supported by the National Natural Science Foundation of China, grant number 22005046; the Fundamental Research Funds for the Central Universities, grant number 2232019D3-41 and 2232020D-03; and the City University of Hong Kong Strategic Research Grant (SRG), grant number 7005105.

### Institutional Review Board Statement
Not applicable.

### Data Availability Statement
Data are not available publically, though the data may be made available on request from the corresponding author.

### Conflicts of Interest
The authors declare no conflict of interest.

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Fabrication of Bimetallic Oxides (MCo$_2$O$_4$: M=Cu, Mn) on Ordered Microchannel Electro-Conductive Plate for High-Performance Hybrid Supercapacitors

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Figure S1. SEM mappings of (a) the CuCo$_2$O$_4$/OMEP electrode; (b) the MnCo$_2$O$_4$/OMEP electrode.
Figure S2. SEM images: (a–d) CuCo$_2$O$_4$ nanostructures fabricated on nickel foam with different magnification.

Figure S3. SEM images: (a–d) MnCo$_2$O$_4$ nanostructures fabricated on nickel foam with different magnification.
Figure S4. XRD patterns of O s1 for (a) CuCo$_2$O$_4$/OMEP and (b) MnCo$_2$O$_4$/OMEP.

Figure S5. (a) CV curves of CuCo$_2$O$_4$/NF at different scanning rates and (b) charging–discharging curves of CuCo$_2$O$_4$/NF at different current densities after activation.

Figure S6. (a) CV curves of MnCo$_2$O$_4$/NF at different scanning rates and (b) charging–discharging curves of MnCo$_2$O$_4$/NF at different current densities after activation.
Figure S7. charge–discharge curves of the newly fabricated OMEP, Co₃O₄/NF, CuCo₂O₄/OMEP and MnCo₂O₄/OMEP electrode at a current density of 5 mA cm⁻².