Electronic supplementary information

In-situ fabrication of porous CF@Cu₂O@NiMn₂O₃ heterostructures as integrated electrodes for photo-supercapacitors

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Experimental section

All chemicals used in this study were of analytical grade and purchased from Aladdin. They were used without any further purification. The details of the chemicals are as follows: Sodium sulfate anhydrous (Na₂SO₄, \geq 99%), Sodium hydroxide (NaOH, \geq 99%), Ammonium persulfate ((NH₄)₂S₂O₈, \geq 98%), Potassium hydroxide (KOH, \geq 85%), Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, \geq 98%), Ammonium fluoride (NH₄F, \geq 96%), Urea (CO(NH₂)₂, \geq 99%), Manganese(II) chloride tetrahydrate (MnCl₂·4H₂O, \geq 99%), and Hydrochloric acid (HCl, 36–38%).

Preparation of CF@Cu(OH)₂

After being cut into 1×1.2 cm² pieces, the copper foam (CF) was successfully ultrasonically treated for 10 minutes in deionised (DI) water, 0.1 M HCl aqueous solution, and anhydrous ethanol. The CF was carefully washed with DI water after each procedure, and it was then dried for 12 hours at 60°C to produce the pretreated CF. To create CF@Cu(OH)₂ nanowire arrays, 6.4 g of NaOH and 3.652 g of ammonium persulfate were dissolved in 16 mL of DI water (Solution A and Solution B, respectively). After that, Solution A was added to Solution B while being continuously stirred until it was completely dissolved. After being immersed in this mixture, the

pretreated CF was left to react for half an hour. Following the reaction, the CF was carefully cleaned with DI water and anhydrous ethanol before being dried for 12 hours at 60°C to produce CF@Cu(OH)₂ NWs arrays.

Preparation of CF@Cu₂O@NiMn₂O₃

A precursor solution was made for the production of CF@Cu₂O@NiMn₂O₃ by dissolving 290.8 mg of manganese chloride tetrahydrate (MnCl₂·4H₂O), 187.2 mg of ammonium fluoride (NH₄F), 301.6 mg of urea (CO(NH₂)₂), and 290.8 mg of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) in 40 mL of DI water. To guarantee total dissolution, the liquid was vigorously stirred for ten minutes. The CF@Cu(OH)₂ NWs arrays were then submerged in this solution, moved into an autoclave lined with polytetrafluoroethylene, and hydrothermally treated for 12 hours at 120°C. After the sample had naturally cooled, it was taken out, thoroughly washed with DI water and anhydrous ethanol, and then dried at 60°C for 12 hours. The final CF@Cu₂O@NiMn₂O₃ composite was obtained by annealing the dried material in a muffle furnace by heating to 350°C at a ramp rate of 1°C min⁻¹ and keeping it there for two hours before allowing it to cool naturally.

Materials characterization

The crystal structures of the produced materials were investigated using X-ray diffraction (XRD, Rigaku D/max 2500) with Cu K α radiation (λ = 0.154 nm). X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha ESCALAB 250XI) assessed the surface chemical composition and oxidation states using an Al K α X-ray source (1486 eV). Both scanning electron microscopy (SEM, Quanta FEG 250) with an energy-dispersive spectrometer (EDS) and transmission electron microscopy (TEM, Titan G2 60-300) with elemental mapping capabilities were utilized to examine sample morphologies. To conduct the probe, monochromatic incident light with a wavelength of λ = 365 nm and an alternating voltage of 0.5 V was used. The material's band gap and flat band potential were described using the Ultraviolet-Visible Diffuse Reflectance Spectrum (UV-Vis, Shimadzu UV-3600).

Electrochemical and photoelectrochemical measurements

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The electrochemical performance of the as-prepared samples was evaluated using an electrochemical workstation equipped with three electrodes (IVIUM, Vertex C. EIS, Ivium Technologies, Eindhoven, The Netherlands). A platinum (Pt) plate was employed as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode in a conventional three-electrode configuration for all electrochemical studies. An aqueous solution of 6 mol KOH served as the electrolyte for all electrochemical tests. Furthermore, a 0.5 mol Na₂SO₄ solution was used for Mott-Schottky analysis. The frequency range for electrochemical impedance spectroscopy (EIS) was 0.01 Hz to 100 kHz. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests were performed at different scan speeds and current densities to evaluate the electrochemical properties. The following equation was utilized to determine the Areal capacitance (C_A) , [1]:

$$C_A = \frac{I \times \Delta t}{A \times \Delta V} \tag{1}$$

Here C_A is the areal capacitance (mF cm⁻²), I (A) is the discharge current, Δt (s) is the discharge time, A (cm²) is the electrode area, and ΔV is the discharge voltage window. The following formula was used to determine the coulombic efficiency (η) from the GCD curve:

$$\eta\% = \frac{t_d}{t_c} \times 100 \tag{2}$$

The charging and discharging times are denoted by t_c and t_d respectively. For the photoelectrochemical tests, a sealed quartz glass cell was used with the same electrolyte and a three-electrode electrochemical configuration. A Perfect Light PLS-SXE300 300 W xenon arc lamp with a 50 W light power and a 60 mm spotlight radius served as the light source. To minimize photothermal effects, cooling water was used to maintain the test cell temperature at 18°C. In the presence of chopped light, photo enhancement measurements including GCD and CV were performed. With a 0.1 V bias and a scan rate of 1 mV s⁻¹, photocurrent in the range of -0.3 to 0.4 V under chopped light in open-circuit conditions was detected using linear sweep voltammetry (LSV).

As shown in Fig. S1a, the XRD pattern of the CF@Cu₂O@NiMn₂O₃ composite was analyzed using standard reference patterns, which confirmed the presence of Cu (JCPDS #04-0836), Cu(OH)₂ (JCPDS #13-0420), Cu₂O (JCPDS #05-0667), and Mn₂O₃ (JCPDS #41-1442). NiMn₂O₃ and NiO, however, do not show distinct peaks, possibly due to their nanocrystalline which reduces diffraction intensity, or their incorporation into the composite matrix, which broadens or overlaps the peaks. However, TEM analysis confirms the presence of NiMn₂O₃ and NiO in the composite, indicating their highly dispersed or nanoscale form (Fig. 1a). The XPS analysis further validates the formation of NiMn₂O₃ by identifying Mn in the 3⁺ oxidation state (Mn³⁺) and Ni in the 2⁺ oxidation state (Ni²⁺) as shown in Fig. S1d and e. Collectively, these findings indicate that NiMn₂O₃ has been successfully integrated into the matrix of CF@Cu₂O.



Fig. S1. (a) XRD patterns of CF@Cu(OH)₂ (I) and CF@Cu₂O@NiMn₂O₃ (II), and (b-f) XPS spectra of survey, Cu 2p, Mn 2p, Ni 2p, and O 1s of CF@Cu₂O@NiMn₂O₃.

The existence of Cu, Ni, Mn, and O in mixed oxidation states is confirmed by the XPS study of $CF@Cu_2O@NiMn_2O_3$. In Fig. S1b, the C 1s peak at 284.0 eV (used for calibration), Cu Auger peaks at 569.3 eV and 556.4 eV, Ni Auger peaks at 773.2 eV and 712.1 eV, and the Ni 1s peak at 1004.2 eV are clearly identified. Cu_2O is indicated by the Cu 2p spectrum's peaks at 933.79 eV (Cu $2p_{3/2}$)

and 953.56 eV (Cu $2p_{1/2}$), as well as shake-up satellite peaks at 941.33 eV and 943.89 eV (Fig. S1c) [2]. The coexistence of Mn³⁺ and Mn⁴⁺, which increases redox activity, is confirmed by the Mn 2p spectra, which display peaks at 642.08 eV (Mn $2p_{3/2}$) and 653.9 eV (Mn $2p_{1/2}$), with deconvoluted components at 646.06 eV and 652.6 eV (Fig. S1d) [3]. Similarly, the presence of Ni²⁺ and Ni³⁺ is indicated by the Ni 2p spectrum's peaks at 855.44 eV (Ni $2p_{3/2}$) and 873.44 eV (Ni $2p_{1/2}$), with satellite peaks at 861.31 eV and 879.4 eV (Fig. S1e) [4]. The binding energies of 531.62 and 529.8 eV can be assigned to Mn-O and Ni-O, respectively (Fig. S1f).



Fig. S2. SEM images of (a-c) CF@Cu(OH)₂ and (d-f) CF@Cu₂O@NiMn₂O₃.

Electrochemical impedance spectroscopy (EIS) was used to perform MS measurements at a fixed frequency of 100 Hz to assess the electrode materials' semiconductor characteristics (Fig. S3a). To make sure that the data accurately represented the intrinsic behavior of semiconductors under equilibrium, the measurements were carried out throughout a potential range of \pm 0.25 V vs the open-circuit potential (OCP). The pure Cu₂O's intrinsic p-type semiconducting behavior was demonstrated by its negative slope in the MS analysis [5]. On the other hand, NiMn₂O₃ exhibited a primarily positive slope in the MS plot. A positive slope in the MS plot is indicative of n-type semiconductor behavior, confirming the inherent n-type conductivity of NiMn₂O₃. It's significant

to observe that the Cu₂O@NiMn₂O₃ heterostructure showed dual-slope properties in the MS plot, with both positive and negative regions This behavior indicates that a built in p-n heterojunction has formed at the contact between Cu₂O and NiMn₂O₃ [6]. The efficient electrical coupling between the two semiconducting components is highlighted by the coexistence of p-type and n-type responses, which modulates the flat-band potential and enhances charge separation across the junction. This shift validates effective charge separation caused by the inherent electric field and shows band bending at the interface, both of which are advantageous for improved photoelectrochemical performance. We have now integrated this explanation into the discussion and experimental part to give a thorough grasp of the MS analysis and its importance in our system.



Fig. S3. (a) Motschottky test and (b) UV curve and the embedded Tauc diagram of $CF@Cu_2O@NiMn_2O_3$, and (c) band gap structures of Cu_2O , $NiMn_2O_3$ and NiO, respectively.



Fig. S4. Photocurrent response of (a) CF@Cu₂O@NiMn₂O₃ and (b) CF@Cu₂O.



Fig. S5. Voc-time response of (a) CF@Cu₂O@NiMn₂O₃ and (b) CF@Cu₂O.

The Voc–time response for both the CF@Cu₂O@NiMn₂O₃ and CF@Cu₂O electrodes under 20 seconds of intermittent light exposure has been added to Fig. S5. Both samples show a shift in Voc toward more positive values during illumination, which is indicative of photo-induced charge separation. The Voc of the CF@Cu2O@NiMn2O3 sample is -422.9 mV in the dark and increased to -420.9 mV under light, while the Voc of the CF@Cu2O sample is -158 mV in the dark and increased to -83.42 mV under light. This difference demonstrates the NiMn₂O₃-coated electrode's improved charge separation and increased photovoltaic response, which are ascribed to the creation of a heterojunction that efficiently inhibits recombination.



Fig. S6. CV curves obtained under dark of (a) $CF@Cu_2O@NiMn_2O_3$ and (b) $CF@Cu_2O$, (c) CV comparison between $CF@Cu_2O@NiMn_2O_3$ (red) and $CF@Cu_2O$ (black) under dark at 20 mV s⁻¹ and (d) CV comparison $CF@Cu_2O@NiMn_2O_3$ under dark and light, respectively.



Fig. S7. The CV curves obtained under light of (a) $CF@Cu_2O@NiMn_2O_3$ (b) $CF@Cu_2O$, respectively.

 Scan rate (mV s ⁻¹)	Dark (F cm ⁻²)	Light (F cm ⁻²)
10	3.03	3.30
20	2.55	2.66
30	2.06	2.25
50	1.51	1.65
100	0.81	0.90

Table S1. The areal capacitance calculated from various scan rates under dark and light, respectively, of the CF@Cu₂O@NiMn₂O₃ sample.

Table S2. The areal capacitance calculated from various scan rates under dark and light, respectively, of the CF@Cu₂O sample.

Scan rate (mV s ⁻¹)	Dark (F cm ⁻²)	Light (F cm ⁻²)
10	0.772	0.778
20	0.648	0.659
30	0.586	0.592
50	0.527	0.541
100	0.422	0.435

The CV curves of the CF@Cu₂O@NiMn₂O₃ electrode under illumination are shown in Fig. S7a, while the CV curves of the CF@Cu₂O electrode recorded under the same light circumstances are shown in Fig. S7b. In comparison to CF@Cu₂O, the CF@Cu₂O@NiMn₂O₃ electrode shows a significantly larger CV loop area and higher current density, which clearly demonstrates an improved areal capacitance and superior charge storage ability. This enhancement is ascribed to both the photo-induced charge separation made possible by visible light and the synergistic redox contributions of the Cu₂O and NiMn₂O₃ components [7]. The creation of a heterojunction between Cu₂O and NiMn₂O₃ facilitates the effective separation and movement of these charge carriers, which are produced by light absorption during illumination. These findings support the critical roles that light and the NiMn₂O₃ layer play in improving charge separation and electrochemical activity, which in turn improves the CF@Cu₂O@NiMn₂O₃ composite electrode's

overall photo-capacitive performance. The areal capacitance values calculated from the CV curves are provided in Tables S1 and S2.

	$R_s(\Omega)$	$R_{ct}(\Omega)$
Dark	0.7627	31
Light	0.7357	24

Table S3. Charge transfer resistance (R_{ct}) and contact resistance (R_s) under dark and light conditions of the CF@Cu₂O@NiMn₂O₃ sample.

The Nyquist plots produced in lighted and dark situations were investigated to determine the effect of light on the interfacial resistance characteristics. The contact resistance (Rs) shows minimal modification under light and dark circumstances, indicating that the thermal effect of lighting is low and does not appreciably influence the inherent conductivity of the electrolyte or electrode/electrolyte interface. The charge transfer resistance (Rct) does, however, significantly drop when illuminated, by 22.58% as compared to the dark environment. A considerable improvement in interfacial charge transfer kinetics brought on by light exposure is reflected in this numerical reduction, despite its seemingly modest appearance [8]. The reason for this improvement is that photo-induced charge carrier production and separation lowers electronhole recombination and promotes more effective charge transport across the electrolyte interface. These results demonstrate that light is essential for lowering the charge transfer resistance and enhancing the photo-responsive electrode's overall electrochemical performance.



Fig. S8. Raman spectroscopy of Cu@Cu₂O@NiMn₂O₃.

We used Raman spectroscopy to verify the synthesized composite's structural makeup. The Cu-O vibrational modes that are characteristic of Cu₂O and indicate its successful creation are responsible for the observed peaks at 152.8 cm⁻¹, 211.7 cm⁻¹, 294.4 cm⁻¹, and 416 cm⁻¹ [9]. The presence of nickel oxide is suggested by the peak at 502.7 cm⁻¹, which correlates to Ni-O vibrations [10]. The existence of manganese oxides in the sample is confirmed by the assignment of the peak at 636.2 cm⁻¹ to Mn-O vibrations [11]. Together, these findings show that CuO, Ni, and Mn-based oxides can be successfully integrated into the composite, substantiating the structural and compositional claims of the suggested material system.



Fig. S9. XRD results of the Cu@Cu₂O@NiMn₂O₃ electrode after cycling.

Fig. S9 presents the XRD patterns of Cu(OH)₂, Cu, Cu₂O, and Mn₂O₃ in the Cu₂O@NiMn₂O₃ composite. As shown in Fig. S9, XRD analysis of CF@Cu₂O@NiMn₂O₃ after 7500 electrochemical cycles reveals significant phase evolution. Post-cycling, Cu(OH)₂ disappears, likely reduced to Cu₂O or metallic Cu via redox reactions, which helps suppress side reactions. XRD pattern variations after cycling indicate surface rebuilding and phase transformation brought on by extended electrochemical stress. $Cu(OH)_2$ (JCPDS No. 13-0420) corresponding new diffraction peaks appear, suggesting that metallic copper experiences surface hydroxylation as a result of ongoing redox cycling in an alkaline or aqueous electrolyte environment. In parallel, a rise in the strength of Cu₂O peaks indicates that Cu is gradually oxidized to its Cu⁺ state during cycling. On the other hand, the metallic Cu peaks' intensity substantially drops, suggesting either possible surface passivation or partial conversion of Cu into oxide and hydroxide phases. Additionally, the Mn₂O₃ phase exhibits great structural stability under repeated cycling conditions, showing no discernible shift or degradation in its distinctive peaks. Together, these findings show that NiMn₂O₃ provides strong support and structural resilience, which may enhance the electrode's overall electrochemical durability even when Cu-based components experience dynamic phase transitions.



Fig. S10. SEM images of Cu@Cu₂O@NiMn₂O₃ after cycling.

The morphological evolution of the Cu₂O@NiMn₂O₃ heterostructure before and after 7500 electrochemical cycles provides critical understanding into its structural resilience and degradation mechanisms. Initially, the material exhibits a well-defined nanowires architecture (Fig. S10), which maximizes surface area for electrochemical reactions while maintaining mechanical robustness [12]. Post-cycling, a slight increase in nanowire thickness is observed, likely attributed to partial surface oxidation or electrolyte-derived deposition (e.g., formation of a stabilizing solid-electrolyte interphase) [13], which could enhance interfacial charge transfer and active site availability [14]. Simultaneously, localized micro-cracks emerge, primarily due to repeated volumetric stress during redox cycles. These stresses arise from the expansion/contraction of active phases (e.g., $Cu_2O \leftrightarrow CuO$, Mn redox transitions), generating mechanical strain at grain boundaries or interfacial junctions. However, the overall structural integrity remains preserved, emphasizing the heterostructure's ability to accommodate strain without catastrophic failure. This balance between minor surface modifications and crack formation indicated the material's self-adaptive durability, where controlled morphological adjustments mitigate mechanical degradation while maintaining electrochemical activity. The retained nanowire framework, despite cracks, further suggests that the core construction remains intact, ensuring continuous electron transport pathways. These observations align with the material's stable cycling performance, as the cracks are superficial and do not propagate to compromise the entire structure. This behavior exemplifies a crack-tolerant design [6], where

stress dissipation through localized defects preserves macroscopic functionality, a key feature for long-cycle energy storage materials.

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