



Supercapacitive performance of electrodes based on defective ZnO nanorods anchored on graphene nanowalls

Yang Ma^{a,b,*}, Stefanos Chaitoglou^{a,b}, Ghulam Farid^{a,b}, Roger Amade^{a,b}, Rogelio Ospina^{a,c}, A.L. Muñoz-Rosas^a, Enric Bertran-Serra^{a,b,*}

^a Department of Applied Physics, University of Barcelona, C/Martí i Franquès, 1, 08028 Barcelona, Catalunya, Spain

^b ENPHOCAMAT Group, Institute of Nanoscience and Nanotechnology (IN2UB), University of Barcelona, C/Martí i Franquès, 1, 08028 Barcelona, Catalunya, Spain

^c Escuela de Física, Universidad Industrial de Santander, Carrera 27 calle 9 Ciudad Universitaria Bucaramanga, Colombia

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ABSTRACT

Vertical graphene nanowalls (GNWs) have emerged as a highly promising architectural structure, offering a vast surface area teeming with active sites and expediting ion diffusion. In our relentless pursuit of bolstering their specific capacitance, we unveil a groundbreaking supercapacitive augmentation, incorporating defect-engineered ZnO nanorods (ZNRs) branching out from the GNWs. The realization of this hierarchical structure is achieved through a meticulous multi-step process, featuring inductively coupled plasma-chemical vapor deposition, magnetron sputtering, and hydrothermal synthesis. The presence of oxygen vacancy (OV) defects within the ZNRs, induced by argon annealing, has been characterized using X-ray photoelectron spectroscopy (XPS). The emergence of OV defects below the conduction band of the ZNRs results in a narrowing of the bandgap within the hybrid structure, thereby enhancing its conductivity and increasing the reaction sites. The capacity of the ZNRs/GNWs hybrid electrodes were evaluated in an aqueous KOH electrolyte solution, operating within a voltage range of 0.5 V and at a current density of 0.1 mA cm⁻². This assessment yielded an area capacitance of 21.45 mF cm⁻², signifying a 1.5-fold increase in capacitance compared to GNWs grown on graphite sheets. The ZNRs/GNWs hybrid demonstrates remarkable electrochemical performance and exhibits substantial potential for energy storage applications. Our work is expected to offer valuable insights for the enhancement of electrochemical properties in various composite and hybrid materials.

1. Introduction

Supercapacitors are considered to be the ideal energy storage devices to meet the growing demand for electric vehicles and wireless devices [1–3]. Compared with traditional batteries, supercapacitors have higher power density, longer cycle stability, shorter charge–discharge cycles, and improved coulombic efficiency. However, their use as a major energy source to replace batteries has been hampered by their low energy density [4–6]. As a result, there has been a continuous drive towards the use of nanostructured materials that have improved specific capacitance. The majority of the research is primarily concerned with the development of electrode materials such as carbon, conductive polymers and metal oxides. Among these materials, carbon-based options such as activated carbon, carbon nanotubes (CNTs) and carbon aerogels have received considerable attention in relation to energy storage devices [7].

Based on their charge storage mechanism, supercapacitors are

divided into electrochemical double layer capacitors (EDLCs) and pseudocapacitors. EDLCs mainly utilize carbon-based materials as electrodes, in which energy can be stored at the electrode/electrolyte interface through ion adsorption [8,9]. Activated carbon and CNTs are notable examples of EDLCs, thanks to their exceptional conductivity, large surface area and unique nanoscale effects [10,11]. In recent years, graphene has proven to be the most promising material for energy storage applications owing to its excellent electrical and thermal conductivity, outstanding chemical stability, superior mechanical strength and higher specific surface area compared to other carbon materials [12,13]. However, the limited theoretical capacitance of graphene restricts its further applications due to the disruption of graphene's atomic configuration, which significantly affects its thermal, electronic and magnetic properties [14]. Meanwhile, the stacking of flat graphene sheets may have resulted in an underestimation of the specific capacitance of graphene. Therefore, novel approaches are required to tackle

* Corresponding authors at: Department of Applied Physics, University of Barcelona, C/Martí i Franquès, 1, 08028 Barcelona, Catalunya, Spain.

E-mail addresses: ymamaxx147@ub.edu (Y. Ma), ebertran@ub.edu (E. Bertran-Serra).

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physical restrictions like agglomeration which curtails porosity and obstructs the movement of electrolyte ions to concealed areas on the electrode surface. In following studies, researchers discovered that altering the alignment of graphene from horizontal to vertical resulted in a 38 % increase in capacitance at a scan rate of 100 mV s^{-1} , as a result of the greater specific surface area offered by the open upright aligned structure of graphene, which also allows for a more convenient diffusion path for ions [15–18]. Subsequently, vertical graphene nanowalls (GNWs) fabricated by plasma-enhanced chemical vapor deposition (PECVD) technique have subsequently undergone extensive investigation due to their superior electrical conductivity, vast surface area, and three-dimensional composition, making them optimal scaffolds for producing supercapacitor electrodes [19–22]. On the other hand, it is worth noting that pseudocapacitors, which are mainly composed of metal oxides and polymers (e.g., RuO_2 [23], V_2O_5 [24,25], Co_3O_4 [26,27], MnO_2 [28,29], NiO [30,31], and NiCo_2O_4 [32]), have the ability to store energy via fast and reversible faradaic redox reactions within electroactive substances. This typically results in a higher degree of specific capacitance compared to EDLCs [33]. However, the inclusion of a conducting phase, such as a carbon base, is usually required to improve charge transfer due to the relatively low conductivity and poor stability of such metal oxide materials [34]. Additionally, carbon-based materials demonstrate a higher charge storage capacity after the oxidation process, which also enhances their feasibility and stability for composite synthesis in both water and organic solvents [35]. The combination of carbon materials and particular metal oxides exhibits a synergistic effect, fulfilling the essential criteria for new energy storage devices. Composite electrodes, comprising metal oxides alongside carbon materials, provide electroactive substances with the benefits of high electrical conductivity and a significant surface area. Moreover, these electrodes restrict volume changes that may happen during periodic charging and discharging of metal oxides or hydroxides [36]. Nevertheless, the utilization of most metal oxides poses restrictions in terms of high cost and toxicity. Therefore, the production of low-cost supercapacitor electrode materials represents a significant challenge in the field of energy storage. Consequently, it is crucial to investigate alternative materials that would be more suitable for supercapacitor applications. ZnO is a wide bandgap semiconductor material that has garnered significant attention for its potential in energy conversion and storage applications (e.g., gas sensors [37], optoelectronics [38], and solar cells [39]) due to its natural availability, environmental friendliness, reduced cost, enhanced theoretical capacity, proper reversibility, and extended cycling life [40]. It has been also reported that specific capacitance of ZnO can be significantly increased by maintaining an appropriate concentration of oxygen vacancies [41]. This phenomenon is attributed to the increased ion conduction stemming from surface defects [42]. Annealing in inert atmospheres such as argon and nitrogen has been shown to significantly elevate the concentration of oxygen vacancies, resulting in enhanced kinetics for fast electron/ion transfer and the creation of electrochemical sites for Faradaic reactions [43,44]. In 2010, Lu et al. reported a maximum specific capacitance of 61.7 F/g for graphene-ZnO films produced via ultrasonic spray pyrolysis [45], while another report demonstrated a maximum specific capacitance of 146 F/g for G-ZnO nanocomposites. To improve surface morphology and composite structure, Ramli et al. combined functionalized CNTs with graphite nanofibers (GNFs) creating CNTs/GNFs. Subsequently, they introduced zinc oxide nanopowders into this hierarchical structure through a hydrothermal method, and finally obtained CNTs/GNFs/ZnO ternary composites with a specific capacitance of up to 306 F/g [46]. Despite this success, the fabrication process for these nanostructured supercapacitors typically requires costly and intricate procedures. Additionally, further improvements are necessary to enhance their electrochemical performance in terms of specific capacitance and reproducibility.

In this work, we demonstrate the enhanced supercapacitive performance of ZNRs anchored on GNWs hybrid electrodes grown on flexible

graphite for the first time. The GNWs were fabricated by inductively coupled plasma-chemical vapor deposition (ICP-CVD), followed by a thin coating of ZnO seed layer using magnetron sputtering, and finally a hierarchical structure of ZNRs/GNWs was formed by branching ZnO nanorods via hydrothermal reaction. In addition, the annealing process in an argon (Ar) atmosphere resulted in the formation of oxygen vacancies on the surface of metal oxides. This approach led to a substantial improvement in capacitance, primarily due to the synergistic interaction between ZNRs and GNWs. The interlacing ZNRs have facilitated the formation of this hierarchical structure, thus considerably enhancing the accessible surface area and yielding additional pathways for charge transport.

2. Materials and methods

2.1. Preparation of GNWs

Fig. 1 displays a diagram outlining the method of producing the hybrid nanostructure of ZNRs/GNWs. In particular, copper serves as an efficient current collector during electrochemical testing, aiding in the precise measurement and recording of electrochemical properties of the hybrid material. ICP-CVD method was employed to fabricate GNWs, as depicted in Fig. S1, using flexible graphite sheets (Papyex) obtained from Mersen Graphite company with a thickness of 0.02 cm . The synthesis process is comprehensively detailed in previous reports [47,48]. Prior to conducting ICP-CVD, Papyex sheets were cut to a suitable size of $30 \text{ mm} \times 40 \text{ mm} \times 0.2 \text{ mm}$. These sheets were cleaned with isopropanol in an ultrasonic cleaner for 5 min to completely remove organic impurities. After drying, Papyex was loaded into a quartz tubular reactor and the system was subsequently pumped down to a pressure below $3.0 \times 10^{-3} \text{ Pa}$. Upon achieving the predetermined temperature of 750°C , the carbon-containing precursor gas CH_4 was introduced at a flow rate of 10 sccm , and the plasma ignited at an input power of 400 W while maintaining a gas pressure of 400 mTorr within the quartz tube. After 30 min of growth time, both the heating controller and plasma power were switched off, and the CH_4 flow was terminated. The system then underwent a natural cooling process, slowly reverting to room temperature. In order to make the surface of GNWs hydrophilic, thus facilitating the contact with electrolytes, the GNWs grown on Papyex (GNWs/Papyex) were treated in situ with O_2 plasma at room temperature with 40 W power at a pressure of 400 mTorr for 30 s.

2.2. Synthesis of ZNRs on GNWs/Papyex

A ZnO seed layer ($\sim 25 \text{ nm}$ thick) was deposited onto GNWs/Papyex by an RF magnetron sputtering system using a ZnO target (99.9 % purity, Kurt J. Lesker Company). The GNWs/Papyex substrate was placed in a high vacuum sputtering chamber, which was pumped down to a pressure of $3.0 \times 10^{-4} \text{ Pa}$. The sputtering deposition was performed at room temperature with an applied power of 150 W for 210 s, along with a constant Ar flow of 19 sccm to maintain a working pressure of 3 Pa. This ZnO seed layer covered the GNWs surface uniformly, facilitating the growth of ZNRs. Subsequently, the sample was synthesized by hydrothermal method in a precursor solution prepared by dissolving 0.025 M zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and 0.025 M hexamethylenetetramine [$(\text{CH}_2)_6\text{N}_4$, HMTA] in DI water. To fabricate ZNRs of different sizes, the hydrothermal process was conducted at 95°C for duration of 1 h, 1.5 h and 2 h, respectively (labeled as ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h and ZNRs/GNWs/Papyex-2 h). Finally, the as-grown samples were washed several times with DI water and were subsequently annealed in an Ar atmosphere at 400°C for 2 h.

2.3. Material characterization

The morphology analysis was investigated using a field emission scanning electron microscope (FESEM, JEOL JSM-7001F) at 20 kV .

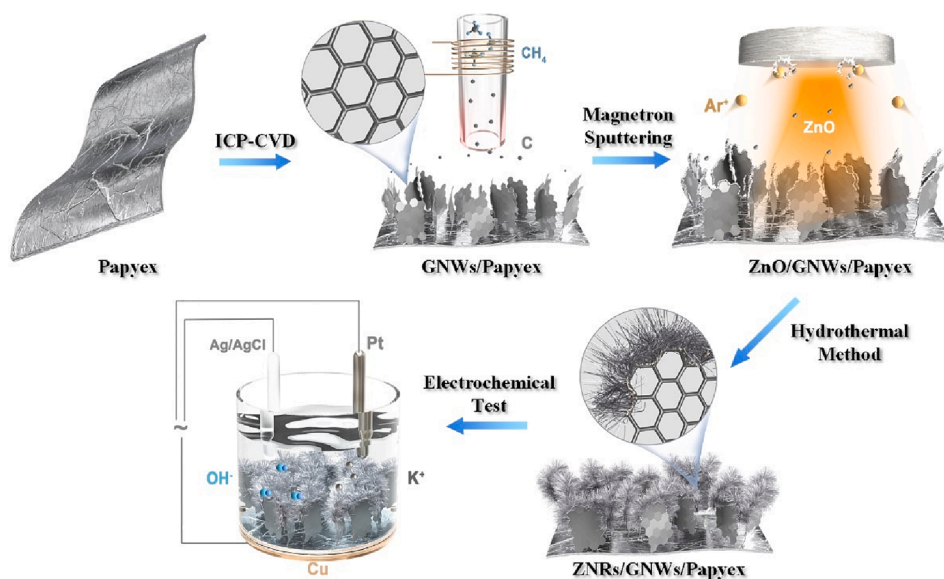


Fig. 1. Schematic illustration of the fabrication of hierarchical structure of ZNRs anchored on GNWs and the electrochemical test based on it.

High-resolution transmission electron microscopy (HRTEM, JEOL 1010) was employed for examining the sample structures at 200 kV. Crystal structures of ZNRs/GNWs/Papyrus were identified by X-ray diffraction measurement (XRD, PANalytical X'Pert Pro MPD) using Cu K α radiation at 50 kV, in a 2θ range from 20° to 80° . Raman scattering and photoluminescence (PL) tests were conducted using a Raman spectrometer (HORIBA France SAS, France) with excitation wavelengths of 532 nm and 325 nm, respectively. Bonding information was recorded via Fourier Transform Infrared (FTIR) spectra using a spectrophotometer (IR PerkinElmer Frontier/ATR diamant/detector DTGS). The wettability of samples was evaluated using a contact angle measurement system (KSV CAM200). X-ray photoelectron spectroscopy (XPS) analyses were conducted using a PHI 5500 Multi-Technique System (Physical Electronics, Chanhassen, MN, USA). This instrument employed a monochromatic X-ray source, specifically the Al K α line with an energy of 1486.6 eV and a power output of 350 W.

2.4. Electrochemical measurements

The electrochemical performance of ZNRs/GNWs/Papyrus hybrid electrodes was evaluated employing a three-electrode system at ambient temperature with a 3 M aqueous KOH electrolyte, using an electrochemical workstation (GAMRY INSTRUMENTS, Interface 1010). The prepared sample can be used as a working electrode without prior treatment. The counter electrode was made of Pt, whereas the reference electrode was composed of Ag/AgCl (3 M KCl internal filling solution). Cyclic voltammetry (CV) was performed at a scan rate of 10 to 150 mV s $^{-1}$ over a voltage range of 0 to 0.5 V [16,18,34]. Galvanostatic charge/discharge (GCD) experiments were performed at various current densities, spanning from 0.1 to 1.0 mA cm $^{-2}$. Electrochemical impedance spectroscopy (EIS) was obtained in the frequency range of 0.1 Hz to 100 kHz with an AC amplitude of 5 mV and an open-circuit potential of 0.15 V. The following equation was used to calculate the specific capacitance from the GCD curve:

$$C_s = \frac{I \times t}{A \times \Delta V} \quad (1)$$

where C_s , I , t , A and ΔV are the specific areal capacitance (F cm $^{-2}$), charge/discharge current (A), discharge time (s), working electrode area (cm $^{-2}$) and voltage drop (V) during discharge, respectively. The C_s of the electrode can also be calculated from the CV test plot using the formula below:

$$C_s = \frac{1}{2v(V_2 - V_1)A} \int_{V_1}^{V_2} IdV \quad (2)$$

where v , A , I , V_2 and V_1 represent the scan rate (mV/s), working electrode area (cm $^{-2}$), current (mA), upper and lower sweeping voltage (V).

3. Results and discussion

FE-SEM analysis was conducted to ascertain the morphology and dispersion of ZNRs within the GNWs matrix. Fig. 2 shows typical FESEM image of the top view of all four samples and the EDS mapping test of ZNRs/GNWs/Papyrus-2 h. In this study, the GNWs are uniformly distributed on the substrate with well-defined edges and nanometer-scale thickness. Fig. 2a illustrates the interleaved structure of the GNWs, which leads to a significant number of cavities ranging from tens to hundreds of nanometers. The interconnected GNWs generally form a three-dimensional network with an open macroscopic structure on the substrate. To investigate the ideal growth duration of GNWs, Fig. S2a–d exhibit the surface morphology of GNWs after various growth times (5, 10, 20, and 30 min). Using these morphology maps, Fig. S2e and Fig. S2f estimate the length and density distributions of GNWs, corresponding to their growth duration. The longest GNWs, approximately 700 nm, are observed at 30 min of growth. The density of GNWs tends to increase with time, reaching saturation density after 30 min. Consequently, GNWs synthesized for 30 min exhibit a larger surface area, enhancing contact area with the electrolyte in electrochemical experiments. Fig. S2g presents a standard FESEM image of a cross-section of GNWs, revealing self-aligned, upright nanowalls around 1 μ m in height.

The broad cavities offer ample room for the deposition of other materials close to GNWs. Fig. 2b–d depict morphological changes of ZNRs anchored on GNWs at various growth periods. The length of ZNRs on GNWs can be regulated by the hydrothermal process reaction time. Fig. 2b shows that the ZNRs/GNWs/Papyrus-1 h is in the growth stage without a distinct rod structure. As the hydrothermal reaction time extends, Fig. 2c displays nanorod-like structures for ZNRs/GNWs/Papyrus-1.5 h. In Fig. 2d, ZNRs conformally cover the top edge and part of the graphene sidewalls, forming highly spiky nanowall hybrid structures with a greater surface area for diverse interface applications, measuring approximately 250 nm in length and 50 nm in diameter (see side view in Fig. S2h).

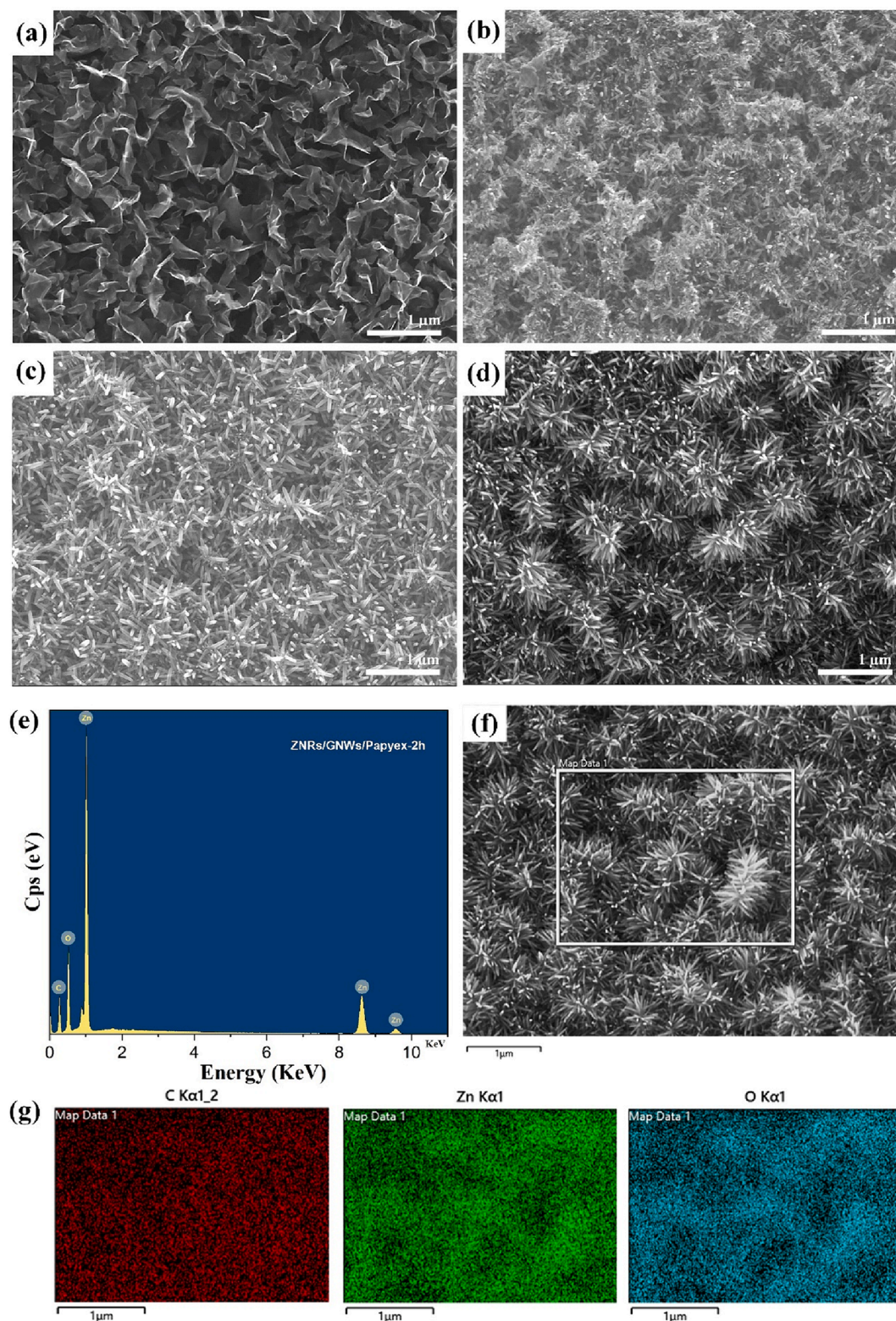


Fig. 2. Typical top-view of (a) GNWs/Papyex, (b) ZNRs/GNWs/Papyex-1 h, (c) ZNRs/GNWs/Papyex-1.5 h and (d) ZNRs/GNWs/Papyex-2 h with size marking, (e) EDS spectroscopy of ZNRs/GNWs/Papyex-2 h confirming of ZnO on GNWs, and elemental mapping of (g) the carbon, oxygen and zinc on the ZNRs/GNWs/Papyex-2 h sample within (f) a rectangular frame.

Energy dispersive X-ray spectroscopy (EDS) technique was conducted to examine the chemical composition of the hybrid structure ZNRs/GNWs/Papyex-2 h, as shown in Fig. 2e. The selected rectangular frame, as illustrated in Fig. 2f, was employed for the acquisition of corresponding elemental mappings, which are depicted in Fig. 2g. In line

with expectations, the spectrum confirms the presence of zinc and carbon, along with elemental oxygen. It is believed that ZnO nanocrystals primarily contribute to the oxygen presence, as the oxygen-containing functional groups associated with the GNWs are expected to be removed during the argon annealing process conducted at high

temperatures. On the other hand, numerous research groups have observed the creation of OV defects in ZNRs when subjected to high-temperature annealing, including at ambient surroundings [49,50]. This is due to the low formation energy of oxygen vacancies in ZnO, leading to a slight oxygen deficiency in normally grown ZnO [51,52]. Moreover, higher temperature annealing within a deprived atmosphere of oxygen causes the elimination of lattice oxygen towards the interstitial site, ultimately creating an oxygen vacancy in accordance with the ensuing deficiency equilibrium:



where V_O represents the lattice oxygen vacancy, Zn represents lattice Zn and O_int represents interstitial oxygen. As the annealing temperature is further increased, the interstitial oxygen becomes unstable and diffuses out of the nanocrystals as a gas phase, as shown in Eq. (4). Therefore, the high-temperature Ar annealing process can lead to considerable OV defects in ZnO nanocrystals, significantly impacting their electrochemical properties. To demonstrate the formation of these structures on the entire substrate, Fig. S3a–c display the SEM images of GNWs/Papyex at low magnification. The figures demonstrate that the GNWs cover the entire Papyex substrate, indicating excellent coverage and consistency. Additionally, Fig. S3d–f exhibit the low-magnification surface morphologies of ZNRs/GNWs/Papyex-2 h composites. The spiny ZNRs were uniformly grown on the surface of the GNWs by the hydrothermal method without stacking, which significantly increased the surface area of the ZNRs. Moreover, Fig. S3g–i show the physical images of Papyex substrate, GNWs/Papyex, and ZnO/GNWs/Papyex-2 h hybrids, respectively. The homogeneously distributed colors on the surface of GNWs/Papyex and ZnO/GNWs/Papyex hybrids confirm the formation of large-area vertical GNWs and ZNRs structures.

Fig. 3 presents the comparison of the XRD patterns of GNWs/Papyex, ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h, and ZNRs/GNWs/Papyex-2 h.

A reflection is present near 26.31° (002) for all samples, indicating the presence of graphitic carbon with a hexagonal structure (JCPDS: 00–001–0640). The 2θ peaks at 34.5° and 36.3° correspond to the (002) and (101) crystal planes of ZnO, respectively, in accordance with JCPDS card no. 00–036–1451. The ratio of peak heights between (002) and (101) increased as the growth time progressed, indicating that the ZNRs

exhibit c-axis orientation near-perpendicular to the GNWs. The XRD results demonstrate polycrystallinity in the ZNRs, indicating the presence of multiple crystal orientations or grains. Each grain may possess its own crystal orientation, resulting in an overall XRD pattern. FTIR measurements were used to provide valuable information regarding the molecular composition, structure and bonding characteristics of hybrid samples, represented in Fig. S4. The GNWs/Papyex composite displayed no distinctive band of wurtzite ZnO in the range of 450 to 550 cm^{-1} . However, in the remaining hybrid materials (ZNRs/GNWs/Papyex), evident broad bands are observed in this specific range. The peak at 497 cm^{-1} represents the Zn–O stretching vibration of hexagonal ZnO. This peak is the most intense in the case of ZNRs/GNWs/Papyex-2 h, in comparison to ZNRs/GNWs/Papyex-1 h and ZNRs/GNWs/Papyex-1.5 h. The increased crystalline size in ZNRs/GNWs/Papyex-2 h, attributed to prolonged growth time, is the reason for the increase of Zn–O bonds.

Raman spectroscopy serves as a valuable tool for the assessment of graphene quality and the characterization of well-organized ZNRs within the composite nanostructure. The first- and second- order Raman spectroscopy of the carbon material shows strong peaks at around 1582 cm^{-1} (G band) and approximately 1350 cm^{-1} (D band), associated with C–C stretching mode and diverse lattice defects [53,54], respectively. Furthermore, the emergence of the 2D band at 2700 cm^{-1} signifies a second-order process derived from the D mode. Fig. 4a illustrates the Raman spectra acquired from GNWs/Papyex, ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h, and ZNRs/GNWs/Papyex-2 h using a 532 nm laser. All the samples exhibit characteristic D, G, and 2D peaks that typify the graphite structure. The elevated D peaks observed in these four samples are associated to disorder stemming from a considerable amount of graphene edge, sp^3 -bonded C–H species, and the presence of amorphous carbon. Detailed Raman spectral parameters for all samples were extracted from Fig. 4a and summarized in Table 1. The $\text{I}_\text{D}/\text{I}_\text{G}$ intensity ratio in Raman spectroscopy is a common indicator of defects in graphene [55]. According to Table 1, the $\text{I}_\text{D}/\text{I}_\text{G}$ values of the three ZNRs/GNWs/Papyex hybrids are lower than that of the GNWs/Papyex, implying a lower presence of defects in GNWs. This observation may be ascribed to the influence of heat treatment in an oxygen-depleted atmosphere, which mitigates structural defects in both GNWs and ZnO while augmenting the electrical transport properties of ZNRs [41]. The comparable $\text{I}_\text{D}/\text{I}_\text{G}$ values within the ZNRs/GNWs/Papyex hybrids provide evidence that the growth process of ZNRs does not harm the structure of GNWs. Additionally, an estimation of the number of graphene layers in GNWs can be determined by the ratio of peak intensities between the 2D and G peaks ($\text{I}_{2\text{D}}/\text{I}_\text{G}$) and full width at half maximum of 2D band ($\text{FWHM}_{2\text{D}}$). As tabulated in Table 1, the low $\text{I}_{2\text{D}}/\text{I}_\text{G}$ values across all samples corroborate the presence of multiple four or five graphene layers within the GNWs [56].

Raman scattering reaches its maximum efficiency when the incident laser wavelength is aligned with the electronic or vibrational transitions in the material. However, when using a 532 nm laser (green spectrum), there may be limits to its resonance with prominent vibrational modes within the ZNRs, resulting in reduced intensity or absence of Raman scattering signals, as shown in Fig. 4a. In the context of ZnO, the optimal excitation wavelength typically lies around 325 nm , where the material displays a pronounced resonance phenomenon with its optical phonon mode. Fig. 4b illustrates the Raman spectra of GNWs/Papyex, ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h, and ZNRs/GNWs/Papyex-2 h. These spectra were obtained utilizing a 325 nm laser source, covering the spectral range from 350 to 1300 cm^{-1} . A significant peak at approximately 439 cm^{-1} is present in all spectra (except for GNWs/Papyex), which serves as a clear indicator of the characteristic Raman mode $\text{E}_2(\text{H})$ associated with ZnO, representing the vibrational oscillations of oxygen atoms within the ZNRs. To eliminate the influence of background noise, we increased the power of the incident light during the Raman test as the intensity of the $\text{E}_2(\text{H})$ peak was very weak. The corresponding enhanced Raman spectra of GNWs/Papyex and ZNRs/GNWs/Papyex-2 h can be found in Fig. S5. The Raman mode $\text{E}_2(\text{H})$

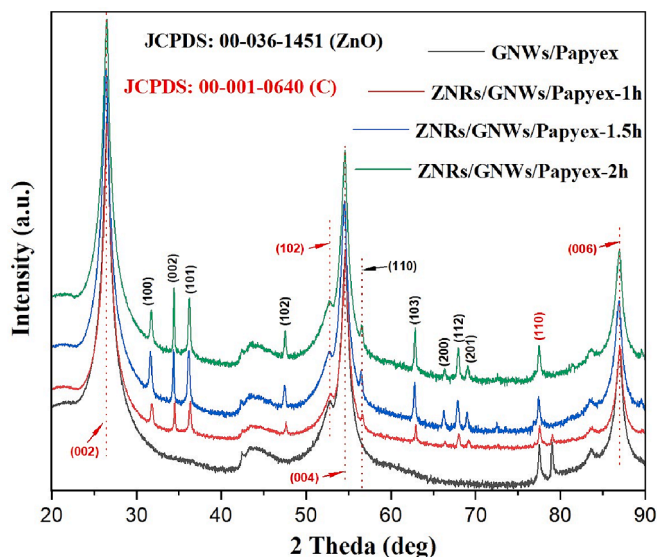


Fig. 3. XRD spectra of GNWs/Papyex and ZNRs/GNWs/Papyex hybrids.

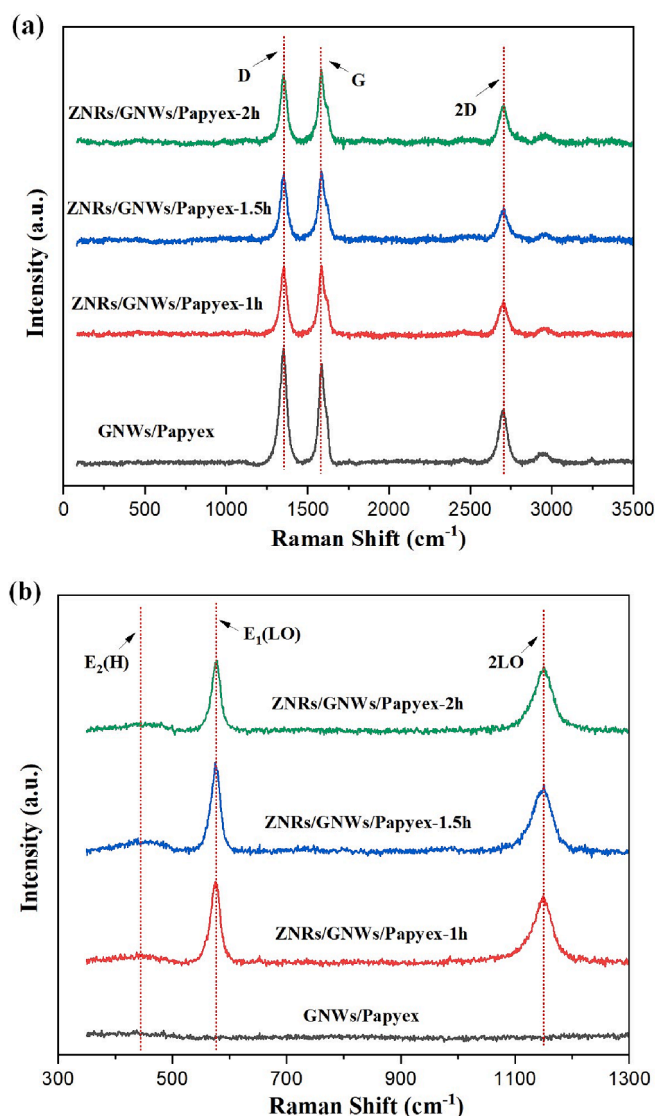


Fig. 4. Comparison of the Raman spectra for GNWs/Papyex, ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h, and ZNRs/GNWs/Papyex-2 h using 532 nm (a) and 325 nm (b) solid-state lasers, respectively.

Table 1

Summary of the Raman spectral parameters of all the samples.

Sample	ω_D (cm^{-1})	ω_G (cm^{-1})	ω_{2D} (cm^{-1})	I_D/I_G	I_{2D}/I_G	FWHM_{2D} (cm^{-1})
GNWs/Papyex	1351.21	1586.69	2700.00	1.16	0.53	62.14
ZNRs/GNWs/Papyex-1 h	1354.40	1585.14	2701.09	0.97	0.49	66.19
ZNRs/GNWs/Papyex-1.5 h	1354.40	1583.60	2703.79	0.95	0.47	63.44
ZNRs/GNWs/Papyex-2 h	1349.62	1582.05	2702.44	0.94	0.51	64.81

associated with ZnO, representing the oxygen atoms in the ZNR, is clearly indicated by the significant peak at approximately 439 cm^{-1} in ZNRs/GNWs/Papyex-2 h. However, this peak is not present in GNWs/Papyex, as they do not contain ZnO. The Raman modes observed at approximately 577 cm^{-1} can be confidently attributed to the $E_1(\text{LO})$ fundamental phonon modes inherent to the hexagonal wurtzite crystal structure of ZnO. The $E_1(\text{LO})$ mode arises from the displacement of the Zn sublattice with respect to the oxygen sublattice, resulting in a net

oscillatory polarization that generates a long-range electrostatic field. This phenomenon in turn leads to the splitting of the polar modes (E_1 and A_1) [57]. In particular, the occurrence of the $E_1(\text{LO})$ mode is closely related to the presence of oxygen vacancies and interstitial Zn [58,59]. The broad peak at around 1149 cm^{-1} is marked as 2LO mode in the high frequency region, which originates from a second-order Raman scattering process involving longitudinal optical (LO) phonons [59]. The Raman analyses suggest the occurrence of oxygen vacancies in the Ar-annealed ZNRs, a finding that is consistent with the following XPS measurements. PL spectra were obtained at room temperature for different samples of GNWs/Papyex, ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h, and ZNRs/GNWs/Papyex-2 h, using a UV laser with an excitation wavelength of 325 nm, as depicted in Fig. S6. In the hybrid structures of ZNRs/GNWs/Papyex, distinctive peaks could be prominently observed in the UV, visible, and near-infrared spectral regions. Notably, the GNWs/Papyex sample did not display any luminescent peaks. A prominent luminescent band, covering wavelengths from 360 to 420 nm, was determined to be the result of near band-edge emission produced by the combination of excitons that occur through electron and hole recombination via collision processes. The broad and weak visible emission band (see the inset of Fig. S6), ranging from 450–700 nm, primarily stems from electron-hole recombination events from intrinsic point defects and surface defects, such as OV defects, formed at deep levels (DL) within the band gap of ZnO [60,61]. Furthermore, the discernible peak detected in the infrared (IR) range (710–820 nm) is thought to be linked to the reduced crystal quality of ZnO nanorods. This aligns with previously published PL results concerning composites of ZnO and carbon nanoparticles [62].

The intricate nanostructure of the hybrid samples underwent further characterization via TEM. In Fig. 5a, a low-magnification TEM image of ZNRs/GNWs/Papyex-2 h reveals a conspicuous attachment of a single ZNR to the GNWs. The nanorods exhibit average length and width dimensions of approximately 250 and 50 nm, respectively. Fig. 5b presents a HRTEM image, where the blue oval region distinctly demonstrates the connection between the ZNR and the GNWs. Simultaneously, the lattice structure obtained by Fast Fourier Transform (FFT) processing of the black selected region in the HRTEM image, as depicted in Fig. 5c and 5f, elucidates the formation of crystalline carbon and ZnO nanocrystals in the proper phase. Fig. 5d and 5g depict the inverse FFT patterns, which unveil the atomic planes within the (002) growth direction of graphitic carbon and crystalline ZnO in ZNRs/GNWs/Papyex-2 h. The strategy chosen for analyzing the crystal structure and potential defects of individual ZNRs is to examine the (002) facet in the TEM. The (002) plane from the ZNR length part in Fig. 5b is perpendicular to the growth axis of the nanorod and provides information on the crystallographic orientation of the nanorod along its length. The crystal plane discussed is particularly sensitive to stacking faults and defects, which makes it a valuable source of information for understanding the structural characteristics of the nanorods. These patterns reveal that the interplanar spacing of carbon and ZnO surface stripes is approximately 0.26 nm and 0.34 nm, respectively. Furthermore, Fig. 5e and 5h provide line profiles for carbon and ZnO, respectively, wherein it is discernible that the cumulative length of 5 crystal planes (002) spacing of carbon measures about 1.705 nm, while the 10 crystal planes (002) spacing of ZnO are approximately 2.591 nm. These values enable the calculation of individual interplanar spacings for carbon and ZnO, which align with the results illustrated in Fig. 5d and 5g. EDS measurements were employed for the chemical composition analysis of the as-prepared samples, as illustrated in Fig. S7a. In this analysis, the presence of ZnO in ZNRs/GNWs/Papyex-2 h was confirmed through the detection of elemental peaks corresponding to Zn and O. Additionally, the carbon signal originated from both the GNWs and the carbon coating film on TEM copper grid. A specific region, highlighted in Fig. S7b, was selected to generate the corresponding elemental map, as presented in Fig. S7c. Notably, the mapping density of carbon was found to be higher on the left side of the selected area compared to the right side. This disparity can be attributed

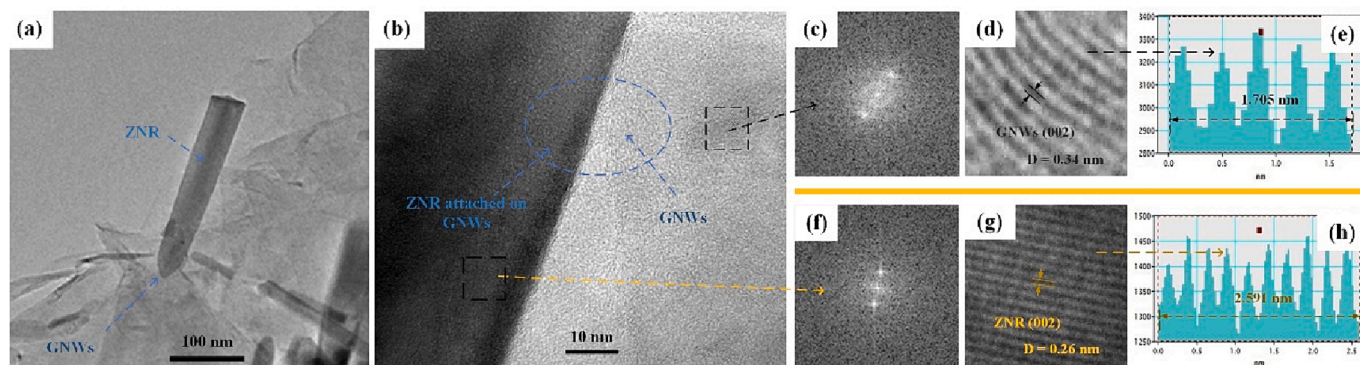


Fig. 5. (a) Low-magnification TEM images, (b) HRTEM images of single ZNR attached to GNWs, corresponding FFT patterns of the (c) GNWs and (f) ZNR, representing the crystalline (d) carbon C (002) and (g) ZNR (002) planes, showing (e) carbon and (h) ZNR line profiles of ZNRs/GNWs/Papyex-2 h, respectively.

to the presence of both GNWs and carbon coatings film on the left side, whereas only the carbon coating film was present on the right side of the region. HRTEM and elemental analysis outcomes clearly demonstrate the presence of Zn and C elements within ZNRs, establishing a clear attachment of ZNRs to GNWs.

To investigate the necessity and effectiveness of the ZnO seed layer in the subsequent hydrothermal growth of ZNRs, Fig. S8a presents the surface morphology of the ZnO seed layer on the GNWs by magnetron sputtering. The coating is well-defined and uniform, which is essential for the subsequent uniform growth of the ZNRs. The EDS spectrum shown in Fig. S8b confirms the presence of Zn, C, and O elements, providing evidence of the successful deposition of the ZnO seed layer on the GNWs. This step is essential for the synthesis process as it guarantees the appropriate chemical composition for hydrothermal growth. The contrast between the physical view of GNWs without the ZnO seed layer after the hydrothermal reaction (Fig. S8c) and the SEM image of GNWs without the seed layer (Fig. S8d) clearly demonstrates the absence of ZNRs. The ZnO seed layer plays a vital role in directing the growth of ZNRs on GNWs.

The hybrids (ZNRs/GNWs/Papyex-1 h, -1.5 h, -2h), as well as the control samples of GNWs/Papyex, were subjected to XPS analysis. This analytical procedure aimed to ascertain the oxidative state of these materials and assess the existence of OV defects following heat treatment within an Ar atmosphere. Fig. 6a illustrates the XPS survey spectra of ZNRs/GNWs/Papyex hybrids, revealing discernible peaks attributed to Zn, O, and C. The presence of GNWs is indicated by the C peak. Notably, the binding energies associated with Zn 2p and O 1s correspond to the XPS core levels of the matrix elements within the ZnO wurtzite structure. To delve into the bonding characteristics in greater detail, Fig. 6b and 6c display XPS spectra for the Zn 2p and O 1s core levels. Deconvolution of the O 1s spectra for the ZNRs/GNWs/Papyex hybrids reveals three distinct peaks situated at approximately 530.60, 531.65, and 532.75 eV. This asymmetry in the O 1s curve signifies variations in

the oxidation state of oxygen [63]. The predominant peak at 530.60 eV is attributed to lattice oxygen (O_L) within the hexagonal Zn—O bonds of the wurtzite structure [64]. Meanwhile, the intermediate-binding-energy peak (O_V) at 531.65 eV primarily corresponds to oxygen vacancy defects associated with O^{2-} ions within regions of oxygen deficiency in the ZNRs matrix [65,66]. This is because an oxygen vacancy constitutes a crystallographic defect characterized by the absence of an oxygen atom, leading to a localized positive charge from the missing anion. This defect alters the electrostatic environment for adjacent oxygen atoms, exposing them to an intensified electric field from Zn cations and thus increasing the effective nuclear charge affecting the core electrons of these oxygens. Consequently, a noticeable increase in the binding energy for the O 1s electrons is observed, evidenced by a shift in the XPS spectrum, with the O_V peak observed at approximately 531.65 eV surpassing the typical binding energy range for fully coordinated oxygen in ZnO (about 530.60 eV). This higher binding energy peak is indicative of oxygen atoms in a lattice with reduced oxygen coordination, aligning with the recognized presence of oxygen vacancies. The high-binding-energy peak at around 532.75 eV is predominantly linked to the presence of weakly bound oxygen on the ZNRs surface, specifically in the form of chemisorbed or dissociated oxygen (O_C) and other oxygen-containing species [66,67]. In summary, the deconvolution of the O 1s spectra reveals two key features: firstly, the presence of Zn—O bonds, indicated by the primary O_L peak, and secondly, structural disorder at the surface in the form of oxygen vacancies. These vacancies may introduce localized defective states within the bandgap, thereby narrowing the bandgap of the ZNRs and ultimately enhancing their electrical conductivity. Conversely, the Zn 2p core level, as depicted in Fig. 6c, was fitted with a doublet situated at approximately 1045.05 eV and 1022.05 eV, corresponding to the $2p_{1/2}$ and $2p_{3/2}$ states. Notably, the disparity in binding energy between Zn $2p_{1/2}$ and Zn $2p_{3/2}$ is 23 eV, and their intensity ratio stands at 1:2, aligning with the established reference for ZnO [68]. Actually, the binding energies of the Zn 2p peaks

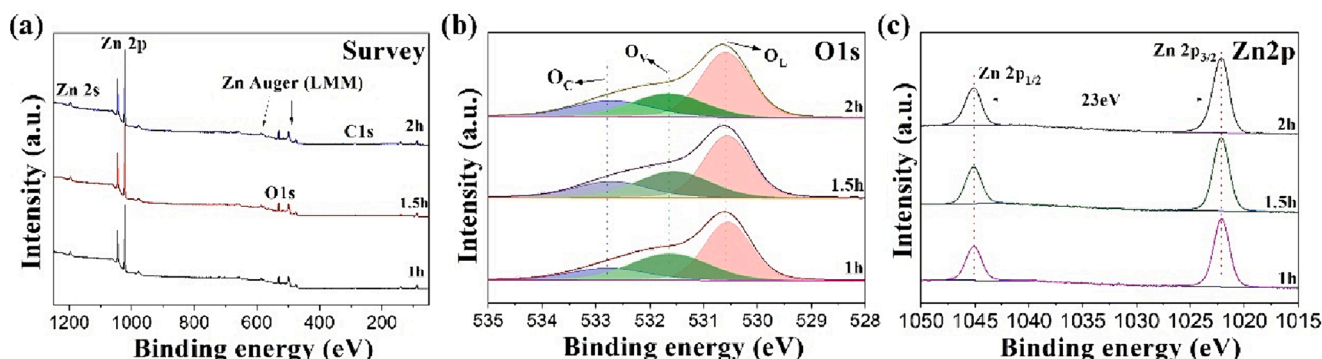


Fig. 6. (a) XPS spectra of ZNRs/GNWs/Papyex hybrids and their enlarge spectrum of (b) O1s and (c) Zn2p.

and their energy differential signify the chemical valence of Zn at the surface of the nanorods, revealing a +2-oxidation state. Moreover, XPS survey spectra of GNWs/Papyex are presented at Fig. S9a, demonstrating the presence of both C and O elements within the GNWs. Simultaneously, Fig. S9b delineates the decomposition of the C 1s XPS spectra of GNWs/Papyex into five Gaussian components, each corresponding to specific chemical bonds: C=C sp^2 (~283.95 eV), C—C (~284.55 eV), C—O (~285.95 eV), C=O (~287.55 eV), and O=C—O (~290.35 eV). These components are well-documented as integral constituents of the GNWs compounds [69].

To prevent the oxygen-containing functional groups in the GNW from affecting the composite capacitance, we analyzed the oxygen content in the GNW after oxygen plasma treatment using an EDS test. The SEM image of the GNW after oxygen plasma treatment is shown in Fig. S10a, with subsequent EDS test points selected at Points 1 and 2. The EDS spectra (Spectrum 1 and Spectrum 2) of Point 1 and Point 2 are shown in Figs. S10b and S10c, respectively. The analysis displays that the oxygen content in the plasma-treated GNW is minimal. This suggests that the O_2 plasma treatment did not significantly alter the overall composition of the graphene material, despite adding oxygen-containing functional groups to the GNW. Table S1 displays the atomic and weight percentages of the elements C and O in the EDS spectra. The EDS data indicate that the O_2 content in the plasma-treated GNW is minimal, with only 0.20 atom % and 0.26 wt% in Spectrum 1, and even lower, at 0.15 atom % and 0.20 wt% in Spectrum 2. The quantitative evidence indicates that O_2 plasma treatment introduces oxygen-containing functional groups to GNW. However, the overall oxygen incorporation is quite negligible. Although these oxygen groups can generate pseudocapacitance via the Faraday reaction, their low concentration implies that their contribution to the total capacitance is relatively insignificant. The pseudocapacitance in composites may primarily originate from OV defect sites within the ZnO structure.

Prior to commencing electrochemical assessments, it is important to establish that GNWs exhibit favorable hydrophilic properties. This characteristic facilitates optimal interaction with the electrolyte, thereby yielding desirable electrochemical performance. Additionally, it ensures effective adhesion of ZNRs to the GNWs during subsequent hydrothermal processes. Specifically, following the synthesis of GNWs on the Papyex substrate, an O_2 plasma treatment is administered to enhance the surface wettability of GNWs. Fig. S11a illustrates the GNWs prior to oxygen plasma treatment, where the water droplets deposited on the GNWs surface exhibit an approximately 90° contact angle with the base plane, indicative of poor hydrophilic properties. In contrast, Fig. S11b depicts the sample post-oxygen plasma treatment, manifesting a significantly reduced contact angle with water droplets (approximately 11.3°). This observation highlights the significant increase in hydrophilicity imparted to the GNWs by the O_2 plasma treatment, demonstrating its effectiveness as a technology for improving the hydrophilicity of material surfaces.

The structural integrity of GNWs is not compromised by O_2 plasma treatment. To confirm this, we conducted a comprehensive analysis with and without plasma treatment. Figs. S12a and S12b display the FESEM images of the GNWs treated with no-oxygen plasma. Compared with the GNWs treated with O_2 plasma (as shown in Fig. 2a), the surface morphology of the GNWs is smooth and homogeneous, and both are highly similar and structurally intact. No holes were detected on the GNW surfaces before or after plasma treatment. To assess whether the O_2 plasma treatment introduces additional defects to the GNWs, we analyzed the Raman spectra of three distinct regions of the GNWs without O_2 plasma treatment, as illustrated in Fig. S12c. The I_D/I_G intensity ratio in Raman spectra is a widely used indicator of graphene defects. In the three selected regions (GNWs/Papyex-1, GNWs/Papyex-2, and GNWs/Papyex-3), the I_D/I_G intensity ratios are all approximately 1.1. This is similar to the I_D/I_G intensity ratio of 1.16 for GNWs treated with O_2 plasma (refer to Table 1). Therefore, the O_2 plasma treatment has little effect on the defects of GNWs. Although GNWs

theoretically have good double capacitance properties, in practice, these properties are only fully demonstrated when GNWs have high hydrophilicity, allowing for full contact between the active material and the aqueous electrolyte. The improvement of wettability promotes ions to enter the surface of the electrodes more efficiently, expanding the contact area between the electrolyte and the GNWs. In turn, this enhances the specific capacitance of the GNWs. Fig. S12d displays the actual GNWs sample treated with oxygen-free plasma. The hydrophobicity of the GNWs is evident as the electrolyte only remains at the top edge and cannot penetrate the three-dimensional mesh structure. This non-full contact limits the utilization of the large surface area of GNWs, ultimately restricting the capacitance of the GNWs.

It is conventionally posited that thermal treatment conducted within an oxygen-depleted environment engenders a reduction in the structural defects exhibited by GNWs and ZNRs, concomitant with an enhancement of the electrical transport properties inherent to ZNRs. This improvement in electrical transport exerts a profound influence on the electrochemical characteristics of these materials. Consequently, our research systematically examined the GCD and CV profiles of GNWs/Papyex, ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h, and ZNRs/GNWs/Papyex-2 h, with the application of a 3 M KOH electrolyte. The 3 M KOH electrolyte provides sufficient ionic conductivity for efficient electrochemical reactions while maintaining a controlled experimental environment. More importantly, it can provide suitable Faraday reaction rates for redox as well as keep good compatibility with ZNRs during redox reactions. To demonstrate the enhanced electrochemical properties of the ZNRs/GNWs hybrid electrode, Fig. 7a depicts the GCD curves of these configurations at a current density of 0.1 mA cm^{-2} . Notably, the GCD profile of ZNRs/GNWs/Papyex-2 h deviates from the typical triangular shape, indicating the coexistence of electric double layer capacitance and pseudocapacitance processes. Furthermore, the ZNRs/GNWs/Papyex-2 h hybrid electrode displays a prolonged charge and discharge duration compared to the other electrodes. In Fig. 7b and S13, CV curves for GNWs/Papyex, ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h, and ZNRs/GNWs/Papyex-2 h hybrids are presented at various scan rates. The lack of symmetry in the electrode curves likely arises from the combination of electric double layer capacitance and pseudocapacitance, both contributing to the overall capacitance, consistent with observations from the GCD curve. At a scan rate of 10 mV s^{-1} , the changes in current between the CV curves are subtle, and the differences in capacitance between hybrid samples may not be immediately apparent. To address this, the Eq. (2) is used to calculate the capacitance of GNWs/Papyex, ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h, and ZNRs/GNWs/Papyex-2 h, which were found to be 10.98, 12.61, 15.24, and 18.62 mF cm^{-2} , respectively. These values suggest that the energy storage behavior of the ZNRs/GNWs/Papyex-2 h material is superior to that of the other three samples. This could be attributed to the increase in Faraday active sites resulting from a longer hydrothermal growth time. It is important to note that small variations in current may be obscured by the scaling and overlapping of the CV curves. However, upon calculating the capacitance values of the composites, it is evident that even small differences in current between the samples are not negligible and have a significant impact on the electrochemical capacitance of the hybrid electrodes. Fig. 7c presents a comparison of the specific capacitance calculated from GCD curves for all tested samples at different current densities. The delivered capacitances for GNWs/Papyex, ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h are 14.48, 17.48 and 19.91 mF cm^{-2} respectively, at a current density of 0.1 mA cm^{-2} . Remarkably, the ZNRs/GNWs/Papyex-2 h hybrid electrode exhibits the highest capacitance, reaching an impressive value of 21.45 mF cm^{-2} , which is 1.5 times greater than that of GNWs/Papyex. The decline in discharge capacitance shows a consistent pattern as the current density increases. This trend could potentially be attributed to the limited ion penetration at the entrances of the nanopores, a consequence of rapid potential changes. The GCD curves of these 4 samples at various current densities are illustrated in Fig. S14.

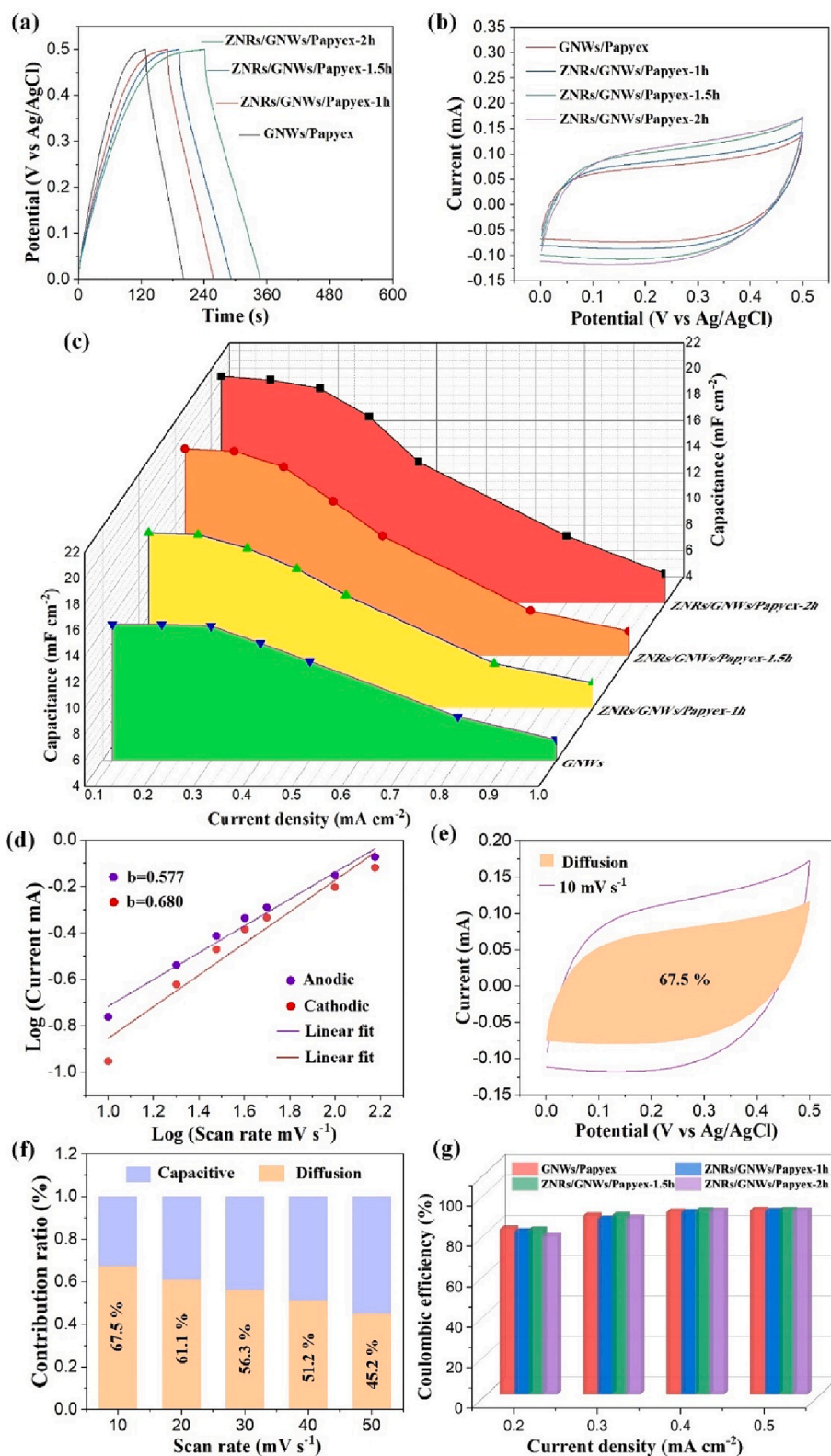


Fig. 7. (a) GCD curves of GNWs/Papyex, ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h, and ZNRs/GNWs/Papyex-2 h at the current density of 0.1 mA cm⁻², (b) CV curves of GNWs/Papyex, ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h, and ZNRs/GNWs/Papyex-2 h at a scan rate of 10 mV s⁻¹, (c) specific areal capacitances of all the samples at various current densities calculated from discharge curves, (d) log(*i*) versus log(*v*) plots of the current peaks at different scan rates, (e) diffusion contribution, (f) the normalized diffusion contribution proportion at each scan rate, and (g) Coulombic efficiency during constant current charge and discharge at various current densities for different electrodes.

The improved performance of the ZNRs/GNWs/Papyex-2 h hybrid can be explained as follows based on these results:

- (i) GNWs typically assemble into a three-dimensional network, exhibiting an expansive open macroscopic configuration on the substrate. The generous void spaces within this framework provide abundant deposition sites for the incorporation of ZNRs (spiky nanorod structures) onto the GNWs. As a consequence, the hierarchical structure of ZNRs/GNWs, inherits the open and porous structure attributes characteristic of the GNWs. This configuration is marked by reduced inter-nanowall distances and an augmented effective surface area. The increase in the effective surface area results in a larger interface for interaction with the electrolyte, consequently enhancing the specific capacitance.
- (ii) This enhancement can be attributed to the capacitance generated through a synergistic interplay between the bilayer behavior of the highly conductive GNWs and the pseudocapacitance associated with the ZNRs.
- (iii) The extended growth duration of the ZNRs and subsequent high-temperature annealing in an Ar atmosphere result in the creation of a substantial number of OV defects within the ZNRs, thereby providing abundant reaction sites. Simultaneously, the conductivity of ZNRs is significantly amplified, leading to an improved carrier transport mechanism during the charging and discharging processes.

The investigation of response dynamics, involving the comparison of peak current (i) and scan rate (ν), was carried out through examination of the following equations:

$$i = a\nu^b \quad (5)$$

$$\log(i) = \log(a) + b \log(\nu) \quad (6)$$

where a and b are both constants. Typically, the parameter b , varying within the range of 0.5 to 1.0, serves as a significant factor for assessing the charge storage mechanism. It can be ascertained by examining the slope of the $\log(i)$ versus $\log(\nu)$ plot. The contribution of capacitance in a semi-infinite liner is characterized as diffusion-controlled when b converges to 0.5, and surface-controlled when b approaches 1.0 [70,71]. Especially, the b values for the cathodic and anodic peaks observed in the context of the ZNRs/GNWs/Papyex-2 h electrode were determined to be 0.68 and 0.57, respectively (as shown in Fig. 7d). This finding suggests that the behavior of hybrid electrode is predominantly governed by a diffusion process. Moreover, the following equation can be employed to quantify the contribution rates of both capacitance and diffusion behavior.

$$i(\nu) = k_1\nu + k_2\nu^{0.5} \quad (7)$$

where k_1 and k_2 represent constants associated with capacitive and diffusion-controlled processes, respectively [72,73]. By calculating the values of k_1 and k_2 , it becomes possible to discern the contributions of the diffusion-controlled and capacitive processes at a specific potential. Fig. 7e presents the response curve depicting the relationship between voltage and diffusion current (illustrated by the orange area) and the CV curve for the ZNRs/GNWs/Papyex-2 h at a scan rate of 10 mV s⁻¹. The diffusion capacitance contribution is observed to be 67.5 % at this scan rate. The evaluation of diffusion contribution within the context of ZNRs/GNWs/Papyex-2 h is attained by differentiating the energy storage modes at different scan rates, illustrated in Fig. 7f. Specifically, at a scan rate of 10 mV s⁻¹, the diffusion contribution constitutes 67.5 % of the total, signifying the prevalence of a diffusion-controlled energy storage mechanism. Conversely, at a higher scan rate of 50 mV s⁻¹, the diffusion contribution decreases to 45.2 %, indicating the predominance of capacitive behavior. This reduction in diffusion control mechanism's contribution with increasing scanning speed is attributed to the fact that

at higher scan rates, the rate at which K⁺ and OH⁻ ions become incorporated or disengaged cannot match the rapid scanning rate, leading to a restricted diffusion-controlled process. It should be clarified that although the double layer capacitance and the Faraday pseudocapacitance contribute differently to the total capacitance at different scan rates, both forms of capacitance are essential to the electrochemical performance of hybrid composites. The double layer capacitance is enhanced by the high specific surface area and electronic conductivity of the GNWs, while the Faraday pseudocapacitance is enhanced by the OV defect sites of the ZNRs. On the other hand, Figs. S15a and S15b present the b -values for ZNRs/GNWs/Papyex-1.5 h and ZNRs/GNWs/Papyex-1 h, respectively. Notably, these b -values fall within the range of 0.5–1, indicating that the total capacitance of both electrodes results from the combined contribution of surface and diffusion capacitances. When the scanning rate is set at 10 mV s⁻¹, the CV curves representing the diffusion-contributions of ZNRs/GNWs/Papyex-1.5 h and ZNRs/GNWs/Papyex-1 h are displayed in Figs. S15c and S15d, revealing diffusion-controlled percentages of 64.3 % and 61.7 %, respectively. These percentages are slightly lower than the diffusion control contribution of ZNRs/GNWs/Papyex-2 h electrodes, which exhibits a diffusion control percentage of 67.5 %. Furthermore, Fig. S15e and S15f illustrate the trends in diffusion control occupancy for ZNRs/GNWs/Papyex-1.5 h and ZNRs/GNWs/Papyex-1 h, respectively, at each scan rate. A comparison with the diffusion control percentage of ZNRs/GNWs/Papyex-2 h electrodes indicates that, at the same scan rate, the ZNRs/GNWs/Papyex-2 h electrodes exhibit the highest diffusion control contribution, the ZNRs/GNWs/Papyex-1.5 h electrodes rank second in terms of diffusion control percentage, and the ZNRs/GNWs/Papyex-1 h electrodes exhibit the lowest diffusion control percentage. This outcome can be attributed to the extended growth time of the ZNRs, resulting in a larger contact area between the ZNRs/GNWs hybrid electrode and the electrolyte. This enlarged contact area offers more available sites for the Faraday reaction due to the increased oxygen vacancies, ultimately leading to a higher pseudo-capacitance contribution. Fig. 7g displays the coulombic efficiency of GNWs/Papyex and ZNRs/GNWs hybrid electrodes at various constant current densities. The efficiencies were measured over a current density range of 0.2 mA cm⁻² to 0.5 mA cm⁻². Specially, the Coulombic efficiency represents the ratio of charge extracted during discharge to charge stored during charging. When the Coulombic efficiency of close to 100 % indicates minimal energy loss and excellent reversibility of the charge/discharge cycle. It can be seen that all electrodes maintain a coulombic efficiency of approximately 90 % across the current density ranges of 0.3, 0.4, and 0.5 mA cm⁻², indicating their strong charge storage capability and good rate performance. These findings highlight the potential of nanostructured ZNRs/GNWs hybrids to enhance the electrochemical performance of supercapacitors.

To exemplify the significance of the three-dimensional structure of GNWs, Fig. S16 illustrates the CV and GCD profile at a scan rate of 10 mV s⁻¹ and a current density of 0.1 mA cm⁻² for pure Papyex and ZNRs/Papyex-2 h (ZNRs grown directly on Papyex with 2 h), respectively. The capacitance values for Papyex and ZNRs/Papyex-2 h were obtained using Eq. (1) and found to be 4.75 and 6.61 mF cm⁻², respectively. These values were markedly lower than those of the other hybrid electrodes. Examining the inset of Fig. S16b, which includes FESEM images of both specimens, the results indicate that the Papyex possesses a two-dimensional planar composition. Additionally, an important observation arises that the ZNRs deposited on the surface of Papyex display considerable stacking, resulting in a converging surface structure. The stacking phenomenon obstructs the smooth flow of ions, which in turn hinders the effective transportation of electrolyte ions. As a result, this stacking effect does not appreciably improve the specific capacitance. This finding highlights the significance of hybrid structures that can notably enhance the speedy movement of ions and charges during redox reactions by enabling greater interfacial contact [74]. Meanwhile, the surface morphology of ZNRs may be negatively affected by the long

hydrothermal reaction time. Fig. S17 displays SEM images of ZNRs/GNWs hybrids at different magnifications after a 3-hour hydrothermal reaction (labelled as ZNRs/GNWs/Papyex-3 h). The dense ZNRs have completely covered the surface of GNWs due to the excessively long hydrothermal reaction time, resulting in the disappearance of the spiny hierarchical structure of ZNRs/GNWs compared to that of the ZNRs/GNWs/Papyex-2 h hybrid electrode. Due to the high coverage of ZNRs, it will be difficult for the electrolyte to penetrate the ZNRs layer and contact the GNWs during the electrochemical test. As a result, the specific capacitance contribution of the hybrid electrode comes solely from the pseudo-capacitance of the ZNRs, without the participation of the double-layer capacitance of the GNWs.

Fig. S16b in the preliminary draft shows that if only the pseudocapacitance property of ZNRs is utilized, ZNRs/Papyex have a specific capacitance of 6.61 mF cm^{-2} , which is very low. To obtain the ZNRs/GNWs spiky hybrid structure with a large surface area, it is necessary to have fine control over the hydrothermal reaction time. This results in a specific capacitance contribution from the synergistic effect of the interaction of the double-layer capacitance of the GNWs with the pseudocapacitance of the ZNRs. These results underscore the substantial enhancement in capacitive performance achieved through the incorporation of GNWs and the introduction of OV defects within the ZNRs in the hybrid ZNRs/GNWs electrode. Furthermore, it is noteworthy that

the ZNRs/GNWs/Papyex-2 h demonstrates superior electrochemical performance when compared to prior studies utilizing ZnO electrode materials, as indicated in Table S2. The increased capacitance of the ZNRs/GNWs hybrid can be attributed to its unique composite structure:

- (1) Enhanced surface area and porosity: The vertical alignment of GNWs in the composite significantly increases the accessible surface area for electrochemical reactions. Our vertical structure differs from planar graphene or randomly oriented graphene/ZnO composites, as it provides an open and porous network that facilitates ion diffusion and reduces the ionic transport path. This feature is critical for high-rate supercapacitive applications that require rapid charge/discharge cycles.
- (2) Controlled ZnO nanorods growth: The developed synthesis process enables precise control over the growth of ZnO nanorods, allowing for the engineering of OV defects that serve as active sites for Faradaic reactions. These OV defect sites promote pseudocapacitance through redox processes that are not as prevalent in composites with pristine ZnO or less controlled ZnO morphologies.
- (3) Direct electrical pathways: This hierarchical structure guarantees an uninterrupted pathway for electron transport by establishing intimate contact between ZNRs and conductive GNWs. This

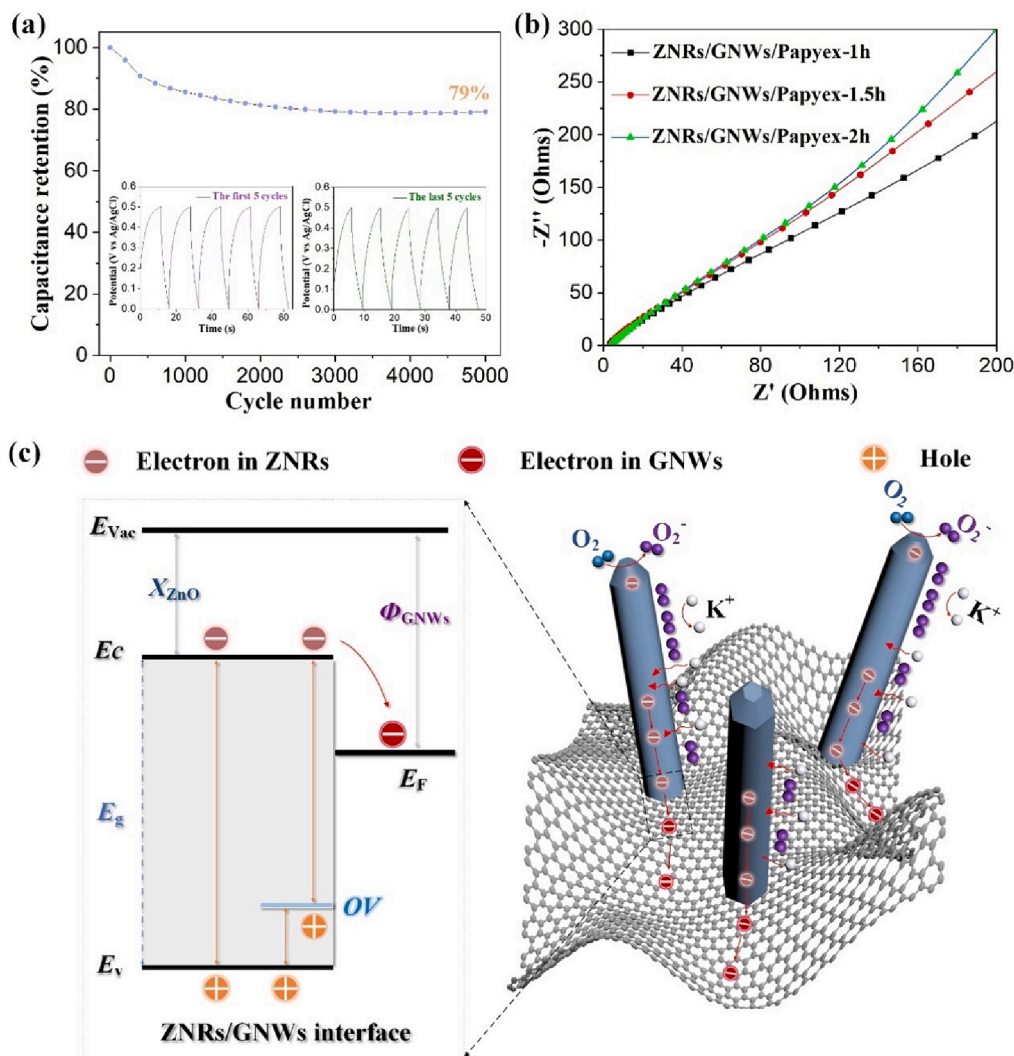


Fig. 8. (a) Cyclic ability test of ZNRs/GNWs/Papyex-2 h measured by the GCD at the current density of 0.8 mA cm^{-2} , and (inset) GCD curves of the first and last 5 cycles of the 5000 GCD cycles. (b) Nyquist plots for ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h, and ZNRs/GNWs/Papyex-2 h, and (c) Energy-band diagram of ZNRs/GNWs system, schematic illustrations of surface chemisorption of molecular oxygen, and carrier transport strategy in the interfacial region of ZNRs/GNWs.

structural advantage reduces internal resistance and improves overall electrical connectivity compared to composites where ZnO and graphene are simply mixed or stacked without a defined interface.

- (4) Synergistic structural effects: The combination of GNWs and ZNRs produces a synergistic effect that exploits the structural advantages of each material; the GNWs provide a robust conductive network, while the ZNRs increase the energy storage capacity through an additional electrochemical mechanism. This hybrid structure creates a synergistic effect between the double layer capacitance of the GNWs and the pseudocapacitance of the ZNRs, resulting in an overall improvement in supercapacitor performance.

In Fig. 8a, the cycling stability of the ZNRs/GNWs/Papyex-2 h electrode is depicted as a function of the number of cycles. This assessment involved a prolonged GCD process conducted over 5000 cycles in a 3 M KOH aqueous electrolyte. Notably, the ZNRs/GNWs/Papyex-2 h hybrid demonstrated a remarkable durability, preserving 79 % of its initial capacitance even after 5000 cycles at a current density of 0.8 mA cm^{-2} . This observation underscores the relatively robust cycling stability of the electrode. Furthermore, the inset in Fig. 8a presents the GCD curves for both the initial five cycles and the final five cycles out of a total of 5000 cycles. Examining the shapes of the GCD cycle curves during the first and last 5 cycles of the sample reveals insignificant modifications, indicating a satisfactory reversibility demonstrated by the hybrid electrode. Fig. S18a shows the FESEM image of ZNRs/GNWs/Papyex-2 h after cyclic stability testing. It can be observed that some ZNRs have detached from the GNWs, which has led to the deterioration of the capacitive performance of the ZNRs/GNWs composite after extensive cycling stability tests. This is due to the direct impact on the Faraday pseudocapacitance contributed by the ZNRs. The efficient electron transport pathway is disrupted when the ZNRs become physically detached from the GNWs conductive network, resulting in a degradation of the electrochemical performance. The reasons for the detachment of the ZNRs could include the mechanical stress during the cycling process and the weak van der Waals forces at the ZNRs/GNW interface that may not withstand the volumetric changes during charge-discharge cycles. Concurrently, the XRD spectrum illustrated in Fig. S18b, resembling the XRD spectrum of the sample prior to the cyclic stability test, confirms that there is no evident lattice damage discernible in the ZNRs/GNWs/Papyex-2 h hybrid after the cyclic stability test.

To access the effect of oxygen vacancies on the electrochemical characteristics of hybrids, electrical properties of ZNRs/GNWs hybrids were examined by EIS measurement conducted at 0.15 V DC bias potential with 5 mV oscillation amplitude spanning a frequency range from 0.1 Hz to 100 kHz. Fig. 8b illustrates Nyquist plots for ZNRs/GNWs/Papyex-1 h, ZNRs/GNWs/Papyex-1.5 h, and ZNRs/GNWs/Papyex-2 h. All of samples exhibit no apparent feature of semicircular arcs at high-frequency regions. In practice, the impedance spectra in the high-frequency domain primarily reflect the electrochemical series resistance (ESR) of the sample, which accounts for the resistances of the cables, between substrate and sample, and of the electrolyte. It can be seen that all ZNRs/GNWs hybrid electrodes present comparable ESR values. In the mid-frequency range, the contribution of charge transfer resistance occurring at the counter electrode/electrolyte interface is observed, with minimal dependence on the properties of the working electrode (ZNRs/GNWs/Papyex). Conversely, impedance spectra in the low-frequency domain are indicative of the diffusion impedance within the electrolyte and are highly contingent on the resistance of the working electrode/electrolyte interfaces [75]. The slope of the impedance curve in the low-frequency range serves as an indicator of the conductive characteristics of the ZNRs/GNWs/Papyex hybrids. Observing Fig. 8b, it becomes evident that ZNRs/GNWs/Papyex-2 h exhibits the steepest slope among all the samples, signifying the most rapid charge transfer and the smallest interfacial resistance in

comparison to the other two samples. This heightened conductivity of ZNRs/GNWs/Papyex-2 h can be attributed to the presence of OV defects. In fact, OV defects are capable of forming shallow donor levels (electron traps) positioned just below the conduction band. These electron traps are credited for increasing carrier density, which subsequently enhances efficient charge carrier transportation within the hybrid electrode [76,77].

The primary characteristic of ZNRs in electrochemical applications, distinguishing them from other pseudocapacitive materials, is their unique ability to facilitate charge storage. During the charge storage process, the presence of exterior oxygen vacancies enhances ion anchoring, while the interior crystalline structure of ZNRs contributes to rapid electron transport owing to its excellent electrical conductivity. Meanwhile, the oxygen vacancies serve as sites for ion penetration, facilitating the occurrence of pseudocapacitive reactions. Specially, OV defects can increase the active sites for redox reactions, which are essential for pseudocapacitance. The presence of such defects on or near-surface regions alters the local electronic structure, creating favorable conditions for charge transfer reactions [78]. Moreover, the reduction in the band gap between the conduction and valence bands is advantageous for augmenting surface conductivity. Meanwhile, many studies using in-situ tests and DFT calculations have demonstrated that OV defects in the hybrid material, as well as changes in the valence state of the metal element during the electrochemical process, significantly contribute to the electrochemical cycling stability and capacity retention of the active material [79–81]. Overall, the pseudocapacitive process in the oxygen vacancies involves the intercalation and deintercalation of K^+ ions within the tunnels of ZNRs, as depicted below:



To gain further understanding of OV defects and their vital role in improving the supercapacitive effect, Fig. 8c illustrates the enhancement mechanisms involved. The OV defects in ZNRs are induced through Ar annealing and act as electron donors below the conduction band minimum, resulting in increased donor density. This is because the vacancies leave two electrons that are weakly bound to the vacancy sites and can be easily excited into the conduction band at relatively low thermal energy in semiconductors. As a result, there is an increase in the n-type conductivity of ZnO [82]. The introduction of OVs results in the creation of localized states in the energy band structure near the valence band edges [83]. Notably, electronic transitions from OV localized states to the conduction band (CB) and from the valence band (VB) to OV localized states play a pivotal role in reducing the bandgap of the ZNRs. Furthermore, with an increase in the density of oxygen vacancies, the OV defects begin to overlap with the valence band edge, causing a shift in the top of the valence band into the forbidden gap [84]. This leads to a further decrease in the bandgap. On the other hand, the electron affinity (χ) of ZNRs is about 4.35 eV and the Fermi level (ϕ) of the GNWs is 4.89–5.16 eV, below the vacuum level [85]. In the ZNRs/GNWs interfaces, the free electrons are inclined to energetically transfer from the conductive band of ZNRs to GNWs, meaning that the ZNRs/GNWs hybrids can transfer the carriers more effectively. More importantly, it has been well established that oxygen molecules in aqueous solution or air can be easily adsorbed onto the exposed surface of ZnO by capturing free electrons from the ZnO ($[\text{O}_2 + \text{e}^- \rightarrow \text{O}_2(\text{ad})]$), resulting in a decrease of conductivity of ZnO [86,87]. The O_2 bound to the surface of ZNRs will function as a hindrance layer, preventing the entrance of K^+ in the solution into ZNRs to carry out the pseudocapacitive reaction as depicted in Eq. (9). The high-temperature Ar annealing treatment makes the ZNRs/GNWs rich in OV defects and greatly improves the electrical conductivity of the ZNRs compared with the unannealed pure ZnO. The enhanced conductivity of ZNRs denotes a substantial augmentation in the mobility of free electrons within the conduction band of ZNRs.

Actually, the addition of OV defects introduces extra electrons into the system, thereby increasing the charge carrier density. Moreover, the presence of OV defects can lead to structural relaxations that reduce scattering centers for charge carriers, effectively enhancing their mobility [88]. Concurrently, the free electrons possess a strong inclination to migrate towards GNWs due to the lower electron affinity potential of ZnO as compared to the work function of GNWs. The high electron mobility and effective carrier transportation greatly reduces the probability of capturing free electrons in the ZNRs by O₂ in solution. Thus, the formation of the O₂⁻ barrier layer is effectively diminished, and the K⁺ ions are more easily accessible to the high-density OV sites in the ZNRs where pseudocapacitive reactions take place, improving the supercapacitive performance of the ZNRs/GNWs hybrids.

4. Conclusions

The conclusions draw from this work encapsulate the successful development of a hybrid electrode, showing remarkable supercapacitive enhancement. This achievement is underpinned by a unique hierarchical nanostructure featuring ZNRs anchored onto GNWs. The fabrication process involved the initial synthesis of GNWs through ICP-CVD, followed by successive stages of magnetron sputtering and hydrothermal growth for the deposition of ZNRs onto the GNWs. A pivotal of enhancement strategy involved the introduction of OV defects through Ar annealing. This deliberate introduction played a crucial role in augmenting the electrochemical properties of the hybrid electrode. The induced OV defects, in conjunction with robust interfacial interactions within the hybrids, significantly improved charge transport during cyclic operations. Moreover, they contributed to an enlarged reactive surface area, thereby elevating the specific capacitance in comparison to the control sample. The composite material, ZNRs/GNWs/Papyex-2 h, exhibited a remarkable 1.5-fold increase in capacitance compared to GNWs/Papyex when assessed at a current density of 0.1 mA cm⁻². This supercapacitive enhancement stems from a confluence of several physicochemical attributes: (i) A synergistic effect resulting from the interplay between the double-layer capacitance of GNWs and the pseudocapacitance of ZNRs. (ii) The high electrical conductivity intrinsic to GNWs, which enhances charge transport. (iii) The nanostructured surfaces of both ZNRs and GNWs, collectively yielding a substantial active surface area, and facilitating additional reaction sites. (iv) Ar annealing, which introduces OV defects in ZNRs, thereby reducing the generation of O₂⁻ barrier layers and improving carrier concentration. This further enhances charge transport properties within the hybrid electrode. In essence, the synthesized hybrid electrode presents a promising avenue for advancing supercapacitor technology, offering improved performance and efficiency through the strategic integration of ZNRs and GNWs. Meanwhile, this work utilizes environmentally friendly techniques for high-performance, sustainable supercapacitor materials. Each method has been historically refined and is industrially scalable. This integration of established technologies highlights our dedication to balancing innovative research with practical environmental applications in the fields of chemical engineering and energy storage.

CRediT authorship contribution statement

Yang Ma: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Stefanos Chaitoglou:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **Ghulam Farid:** Validation, Investigation, Formal analysis. **Roger Amade:** Writing – review & editing, Investigation. **Rogelio Ospina:** Investigation, Formal analysis. **A.L. Muñoz-Rosas:** Methodology, Investigation. **Enric Bertran-Serra:** Writing – review & editing, Supervision, Investigation, Funding acquisition, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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