



Coupled morphology and phase regulation of in-situ grown TiO₂ nanostructures on graphite felt for enhanced redox kinetics in vanadium redox flow batteries

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ABSTRACT

The sluggish electrochemical kinetics of vanadium redox reactions on graphite felt (GF) electrodes remain a critical bottleneck for vanadium redox flow batteries (VRFBs). Herein, phase- and morphology-engineered TiO₂ nanostructures were directly grown on GF via an in-situ hydrothermal method followed by temperature-controlled calcination. By systematically tuning the precursor concentration, vertically aligned one-dimensional TiO₂ nanorods (NR-TiO₂/GF) were identified as the optimal morphology, providing continuous charge-transport pathways, accelerated electrolyte penetration, and abundant accessible active sites. Subsequent thermal modulation (300–600 °C) revealed that annealing at 400 °C (NR400-TiO₂/GF) yielded fine nanorods with an average diameter of ~128 nm while achieving an optimal balance between high crystallinity and a synergistic anatase/rutile heterojunction. The refined nanorod architecture, coupled with surface hydroxyl functionalities and Ti³⁺-associated oxygen vacancies, significantly expedited interfacial charge redistribution and lowered charge-transfer resistance to $R_{ct} = 1.89 \Omega$. Furthermore, NR400-TiO₂/GF exhibited superior redox reversibility across both half-cells, accelerated mass transport, and effective suppression of parasitic hydrogen evolution. In full-cell VRFB tests, the NR400-TiO₂/GF electrode delivered remarkable energy efficiencies of 85.8% at 80 mA cm⁻² and 83.7% at 100 mA cm⁻², outperforming pristine GF and benchmark metal-oxide modifications while shielding the carbon fibers against oxidative corrosion. This work establishes a clear morphology, phase, and performance relationship, providing a potentially scalable strategy for engineering low-dimensional mixed-phase metal oxides toward high-performance energy storage systems.

1. Introduction

Stationary energy storage systems have attracted increasing attention over the past decade because of their important role in grid-scale energy management. They facilitate the integration of renewable energy sources, enhance grid reliability, and improve the utilization of intermittent electricity generation [1]. Among various energy storage technologies, vanadium redox flow batteries (VRFBs) have emerged as promising candidates for large-scale stationary energy storage because of their decoupled power and energy capacities, high operational safety, and long cycle life [2]. Despite these advantages, the widespread

commercialization of VRFBs remains limited by their relatively high capital cost and performance-related losses. Among the key components of a VRFB cell, electrodes play a critical role in determining interfacial redox kinetics, reaction overpotentials, and overall energy conversion efficiency [3].

Three-dimensional (3D) porous graphite felt (GF) is one of the most widely used electrode materials in VRFBs because of its interconnected porous architecture, high electrical conductivity, large electrochemically accessible surface area, mechanical flexibility, and favorable chemical stability in acidic electrolytes [4]. However, pristine GF exhibits limited intrinsic electrocatalytic activity toward vanadium redox

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reactions. In addition, its graphitic carbon surface is generally hydrophobic, which can hinder electrolyte infiltration and limit effective electrode-electrolyte contact within the porous structure. These limitations contribute to sluggish interfacial charge-transfer kinetics and increased polarization losses during battery operation [5]. Consequently, extensive efforts have been devoted to enhancing the electrochemical performance of GF through surface modification strategies, including thermal activation, heteroatom doping, carbon nanomaterial deposition, and metal or metal oxide modification [5,6]. Among these approaches, transition metal oxides have attracted considerable attention because they can improve surface wettability, introduce catalytically active sites, and enhance the interfacial stability of carbon-based electrodes during prolonged cycling [7,8]. In particular, the polar metal-oxygen bonds and surface hydroxyl-containing species of metal oxides can increase their affinity toward polar aqueous electrolytes, while nanoscale surface roughness can further enhance surface wettability. Improved wettability promotes electrolyte contact and penetration within the porous GF structure, facilitating access of vanadium ions to electrochemically active sites and thereby benefiting interfacial redox reactions.

Among various candidates, titanium dioxide (TiO_2) is an attractive electrode modifier because of its tunable crystal phases, chemical stability, environmental benignity, and versatile surface chemistry [9]. In particular, TiO_2 morphology can be tailored through hydrothermal and related chemical synthesis routes by controlling precursor chemistry and reaction conditions, enabling the formation of diverse one-dimensional and hierarchical structures, including nanowires, nanorods, and nanotube-based architectures. Such structural control has been shown to influence surface area, mass transport, interfacial charge transfer, and energy-conversion performance in various electrochemical and energy-related systems [7,8]. Furthermore, crystal-phase engineering provides an additional strategy for regulating the physicochemical and electrochemical properties of TiO_2 [10,11]. The coexistence of anatase and rutile phases can generate mixed-phase interfaces with distinct local structures and surface electronic environments, thereby influencing interfacial charge transfer and catalytic activity [12,13]. Moreover, the phase composition and associated structural defects can alter the availability of surface-active sites and the interaction between TiO_2 and redox-active species. Therefore, the simultaneous regulation of TiO_2 nanostructure morphology and anatase/rutile phase composition provides a promising strategy for optimizing vanadium redox kinetics.

Nevertheless, the simultaneous regulation of nanostructure morphology, phase composition, and interfacial integration on three-dimensional (3D) carbonaceous substrates remains challenging [9–11,14]. TiO_2 -based materials have recently been explored for VRFB electrodes, including nanostructured and composite TiO_2 architectures on graphite felt, with improved electrochemical activity toward vanadium redox reactions being reported. However, previous studies have generally focused on introducing TiO_2 or TiO_2 -containing materials onto GF, while the systematic relationship among TiO_2 morphology, phase composition, surface properties, and vanadium redox kinetics remains insufficiently understood. Conventional electrode modification methods may suffer from particle aggregation, pore blockage, and limited interfacial adhesion between the active materials and carbon substrates [15,16]. Furthermore, many previous studies have focused primarily on modifying a single electrode, particularly the negative electrode, to address the sluggish kinetics of the $\text{V}^{2+}/\text{V}^{3+}$ redox couple and mitigate hydrogen evolution. In comparison, less attention has been devoted to improving the $\text{VO}^{2+}/\text{VO}_2^+$ reaction at the positive electrode and achieving balanced electrochemical performance in full-cell VRFB systems [10–12,15,17]. Therefore, developing a facile, binder-free, and additive-free strategy for the in-situ growth of morphology- and phase-regulated TiO_2 nanostructures directly on GF is highly desirable for enhancing redox kinetics at both electrodes and improving overall VRFB performance [18,19].

Accordingly, the objective of this work is to systematically regulate

the morphology and crystal phase of TiO_2 nanostructures directly grown on GF and to clarify their relationships with surface properties, electrochemical kinetics, and VRFB performance. To achieve this objective, a morphology- and phase-engineering strategy was developed using in-situ hydrothermal growth followed by controlled thermal calcination. By systematically tuning the precursor concentration, distinct TiO_2 architectures, including sea-urchin-like, nanorod-like, and nanoflower-like structures, were synthesized and evaluated. Among these architectures, the nanorod-like TiO_2/GF (NR- TiO_2/GF) exhibited the most favorable electrochemical performance and was further subjected to controlled calcination at 300–600 °C to regulate its morphology, crystallinity, and anatase/rutile phase composition. The optimized NR400- TiO_2/GF electrode exhibited enhanced redox kinetics and reduced charge-transfer resistance, together with improved electrochemical reversibility and mass-transport characteristics. Importantly, the TiO_2/GF electrodes were evaluated in both positive and negative half-cell configurations, demonstrating their applicability to both vanadium redox couples. Consequently, full-cell VRFB tests demonstrated energy efficiencies of 85.8% at 80 mA cm^{-2} and 83.7% at 100 mA cm^{-2} , together with stable cycling performance. Overall, this work establishes a clear relationship between TiO_2 nanostructure morphology, phase composition, and electrochemical performance, providing a facile strategy for engineering mixed-phase metal oxide architectures on three-dimensional carbonaceous electrodes for high-performance redox flow batteries.

2. Experimental

The schematic illustration of the in-situ hydrothermal growth process for synthesizing TiO_2 nanostructures on graphite felt (TiO_2/GF) is depicted in Fig. 1a. Detailed synthesis protocols and experimental characterizations are provided in the Supporting Information.

3. Results and discussion

3.1. Concentration-dependent evolution of TiO_2 nanostructures

3.1.1. Morphological evolution

The morphological evolution of pristine GF and TiO_2/GF electrodes was examined by scanning electron microscopy (SEM), as presented in Fig. 1. The pristine GF exhibited smooth, cylindrical carbon fibers lacking distinct surface features. Following the in-situ hydrothermal growth, the GF surface morphology changed significantly as a function of TiO_2 precursor concentration. At a low concentration of 0.025 M, limited precursor availability resulted in insufficient nucleation and sparse TiO_2 coverage, forming a sea-urchin-like architecture (SU- TiO_2/GF , Fig. 1c). This modest TiO_2 loading provided only a marginal increase in the electrochemically active surface area. When the concentration was optimized to 0.05 M, well-defined nanorods uniformly grew on the GF fibers (Fig. 1d). This nanorod-like architecture (NR- TiO_2/GF) formed a hierarchical, tree-like network that substantially increased the accessible surface area, which is expected to facilitate electrolyte infiltration and provide abundant electrochemically active sites [20]. However, a further increase to 0.15 M led to severe overgrowth and agglomeration. These densely packed TiO_2 structures enveloped the GF fibers in thick, irregular 3D clusters, designated as nanoflower-like TiO_2/GF (NF- TiO_2/GF), as shown in Fig. 1e. [21]. Such excessive aggregation can obstruct effective electron transfer pathways and diminish the overall catalytic efficiency.

Energy-dispersive X-ray spectroscopy (EDS) mapping (Fig. S1) was performed to further verify the elemental composition and spatial distribution of the TiO_2 nanostructures, corroborating the SEM observations. The NR- TiO_2/GF exhibited a distinct and homogeneous distribution of titanium (Ti, green) and oxygen (O, blue), whereas SU- TiO_2/GF showed sparse signals reflecting limited nucleation. Conversely, NF- TiO_2/GF displayed highly intense Ti and O signals,



Fig. 1. (a) Schematic illustration of the in-situ hydrothermal growth process of TiO_2 nanostructures on graphite felt (TiO_2/GF). SEM images of (b) pristine graphite felt (GF), (c) sea-urchin-like TiO_2/GF (SU- TiO_2/GF), (d) nano-rod-like TiO_2/GF (NR- TiO_2/GF), and (e) nano-flora-like TiO_2/GF (NF- TiO_2/GF).

confirming excessive TiO_2 deposition and aggregation. These compositional mappings are in excellent agreement with the SEM analysis, further validating the concentration-dependent growth behavior of the TiO_2/GF electrodes.

3.1.2. Phase composition and crystal structure

The phase composition and crystal structure of TiO_2/GF electrodes with different nanostructures were investigated by X-ray diffraction (XRD), as shown in Fig. 2a. The pristine GF exhibited a dominant broad diffraction peak at $\sim 25.3^\circ$, corresponding to the (002) plane of graphitic carbon. Following the in-situ hydrothermal growth of TiO_2 , characteristic TiO_2 diffraction peaks gradually emerged and became more pronounced with increasing precursor concentration, indicating enhanced

nucleation and crystallization of TiO_2 on the GF. For the SU- TiO_2/GF , only weak TiO_2 -related signals were observed; the diffraction intensity of the minor rutile phase formed was significantly overshadowed by the strong carbon (002) peak, obscuring the rutile (110) reflection. When the precursor concentration is increased to 0.05 M (NR- TiO_2/GF), distinct TiO_2 crystalline peaks appear. In particular, the emergence of a clear rutile (110) reflection at $\sim 27.4^\circ$, together with weaker anatase (101), supports the formation of mixed-phase TiO_2 on the GF surface, consistent with JCPDS No. 21-1276 for rutile TiO_2 and JCPDS No. 21-1272 for anatase TiO_2 [22,23]. The enhanced diffraction intensity and crystallinity agree well with the formation of well-defined TiO_2 nanorod morphology observed by SEM. At a higher precursor concentration of 0.15 M (NF- TiO_2/GF), the diffraction peaks of TiO_2 become

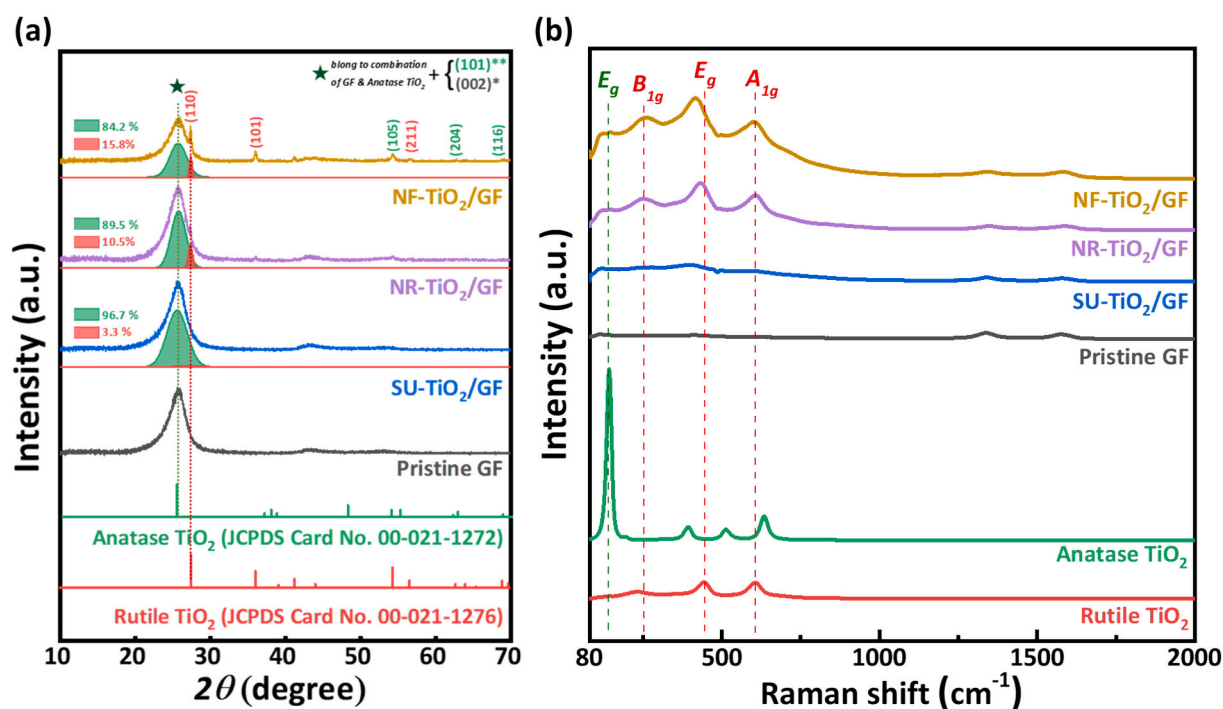


Fig. 2. (a) XRD patterns and (b) Raman spectra of GF and TiO_2/GF electrodes with different nanostructures prepared by in-situ hydrothermal growth, including SU- TiO_2/GF , NR- TiO_2/GF , and NF- TiO_2/GF .

sharp and intense, indicating increased TiO_2 crystallinity and extensive surface coverage on the GF surface. Both rutile and anatase phases are easily identifiable, with rutile- TiO_2 showing dominant peaks at (110), (101), and (211), and anatase- TiO_2 displaying characteristic reflections at (101), (105), and (204) planes, consistent with JCPDS No. 21–1276 and JCPDS No. 21–1272, respectively [24,25]. Consequently, the intense TiO_2 signals from this thick, dense layer significantly weakened and partially obscured the underlying GF (002) peak. Additionally, peak deconvolution was performed to quantify the relative phase composition. The proportion of the rutile phase increased systematically from the SU- TiO_2 /GF to the NF- TiO_2 /GF electrode, revealing a concentration-dependent rutile crystallization behavior under hydrothermal conditions. The combined peak at $\sim 25.3^\circ$, originating from overlapping GF (002) and anatase (101) contributions, becomes increasingly dominated by TiO_2 reflections at higher precursor concentrations. Overall, the XRD analysis clearly demonstrates that increasing precursor concentration enhances TiO_2 nucleation and crystal growth, leading to stronger diffraction intensity, higher rutile fraction, and reduced visibility of the underlying GF structure. To further probe the local structural characteristics and surface crystalline phases, Raman spectroscopy was performed (Fig. 2b). Pristine GF exhibited only the characteristic D and G bands of sp^2 -hybridized carbon at ~ 1338 and $\sim 1577\text{ cm}^{-1}$, respectively. These graphitic features progressively decrease in intensity with increasing TiO_2 loading, reflecting enhanced GF surface coverage by TiO_2 nanostructures. The characteristic Raman modes of anatase (E_g , B_{1g} , $A_{1g} + B_{1g}$, and E_g) and rutile (B_{1g} , E_g , and A_{1g}) were used to identify the TiO_2 polymorphs [26]. For SU- TiO_2 /GF, the Raman spectrum remains dominated by the characteristic carbon D and G bands, with no distinct TiO_2 vibrational modes observed. This observation is consistent with the limited TiO_2 coverage and weak diffraction features identified by SEM and XRD, respectively. For NR- TiO_2 /GF, weak shoulder-like bands emerge near 443 and 604 cm^{-1} , which are assigned to the rutile E_g and A_{1g} modes, while the characteristic anatase E_g mode ($\sim 143\text{ cm}^{-1}$) was barely detectable. In the case of NF- TiO_2 /GF, the TiO_2 -related Raman features were significantly enhanced, with a pronounced rutile A_{1g} band ($\sim 604\text{ cm}^{-1}$) accompanied by broad, low-intensity features near 143 and $395\text{--}512\text{ cm}^{-1}$, which can be associated with anatase TiO_2 modes. The simultaneous appearance of anatase- and rutile-related Raman features indicates the formation of mixed-phase TiO_2 at higher precursor concentrations, consistent with the XRD results. Overall, the Raman analysis supports the concentration-dependent evolution of TiO_2 crystallization and phase composition, particularly the increased contribution of the rutile phase and the emergence of mixed anatase/rutile TiO_2 at higher precursor concentrations.

The surface chemical states and electronic structures of TiO_2 /GF electrodes with different nanostructures were investigated by high-resolution X-ray photoelectron spectroscopy (XPS), as shown in Fig. S2. The C 1s spectra show distinct variations in the carbon environments associated with the different TiO_2 morphologies. SU- TiO_2 /GF exhibits the highest C=C contribution (72.1%), consistent with the relatively sparse TiO_2 coverage, whereas NR- TiO_2 /GF and NF- TiO_2 /GF show lower C=C contributions of 62.8% and 59.3%, respectively, together with increased oxygen-containing carbon species. In the O 1s spectra, the -OH/C-O contribution increases from 20.7% for SU- TiO_2 /GF to 35.1% for NR- TiO_2 /GF, while NF- TiO_2 /GF exhibits 30.2%, indicating differences in the surface oxygen environments associated with the respective morphologies [9,11]. The Ti 2p spectra further reveal predominantly Ti^{4+} states for all three control electrodes. Notably, NR- TiO_2 /GF exhibits the most pronounced Ti^{3+} contribution, with 6.4% and 6.2% assigned to $\text{Ti}^{3+} 2p_{3/2}$ and $\text{Ti}^{3+} 2p_{1/2}$, respectively, corresponding to a total Ti^{3+} fraction of 12.6%. In comparison, NF- TiO_2 /GF shows a lower Ti^{3+} contribution of 10.5%, while no appreciable Ti^{3+} component is observed for SU- TiO_2 /GF [8]. These results indicate that the morphology of the TiO_2 layer influences the surface oxygen configuration and Ti oxidation-state distribution, with the NR architecture exhibiting a comparatively higher fraction of reduced Ti species among

the control electrodes.

3.1.3. Electrochemical performance and kinetics

Prior to evaluating the electrochemical activity, static water contact angle measurements (Fig. S3) were performed. Pristine GF exhibited intrinsic hydrophobicity (122°), which restricts electrolyte infiltration [27]. In contrast, all TiO_2 /GF electrodes exhibited spontaneous wetting, indicating enhanced surface hydrophilicity. This behavior can be attributed to the synergistic effects of surface chemistry and nanoscale morphology. Polar Ti—O surface sites provide strong affinity toward water, while the increased nanoscale roughness amplifies the intrinsic hydrophilicity by increasing the effective solid-liquid interfacial area, consistent with the Wenzel model [14,28]. The resulting super-hydrophilic surface promotes rapid and uniform electrolyte infiltration into the porous GF network, improving electrolyte accessibility and ion transport. Such nanostructured hydrophilic architectures can also facilitate bubble detachment and alleviate mass-transport limitations at elevated current densities [28], thereby contributing to improved electrochemical performance. Consequently, the electrochemical activities toward the $\text{VO}^{2+}/\text{VO}_2^+$ redox couple were assessed by cyclic voltammetry (CV) at 5 mV s^{-1} (Fig. 3a). All electrodes exhibited well-defined redox peaks. Compared with pristine GF, TiO_2 /GF electrodes showed markedly enhanced redox peak currents and reduced peak separation (ΔE), indicating improved redox kinetics and electron-transfer behavior [8]. Notably, the NR- TiO_2 /GF electrode delivered the highest peak current densities ($I_{pa} = -52.03\text{ mA cm}^{-2}$, $I_{pc} = 52.44\text{ mA cm}^{-2}$) with the smallest ΔE (270 mV), suggesting accelerated electron transfer and improved reaction reversibility. This enhancement is likely attributed to the well-defined nanorod architecture, which exposes a high density of active sites and facilitates efficient interfacial charge-transfer pathways [14,29]. The NF- TiO_2 /GF electrode also exhibited a pronounced improvement due to its highly nanoflower morphology, whereas SU- TiO_2 /GF showed only moderate enhancement owing to limited accessible catalytic centers [30]. The overall electrochemical activity followed the trend of NR- TiO_2 /GF > NF- TiO_2 /GF > SU- TiO_2 /GF > pristine GF.

3.1.4. Interfacial charge-transfer kinetics

Electrochemical impedance spectroscopy (EIS) further investigated the charge-transfer kinetic behavior of the electrodes (Fig. 3b). Nyquist plots revealed a decrease in charge-transfer resistance (R_{ct}) following the in-situ growth of TiO_2 on GF, as summarized in Table 1. Among TiO_2 /GF electrodes, NR- TiO_2 /GF exhibited the lowest R_{ct} of $2.39\ \Omega$, highlighting the superior interfacial charge-transfer capability enabled by the nanorod structure. NF- TiO_2 /GF and SU- TiO_2 /GF showed intermediate R_{ct} values of 3.36 and $5.29\ \Omega$, respectively, which is consistent with their surface morphologies and varying degrees of coverage. Furthermore, the fitted double-layer capacitance (C) increased following TiO_2 incorporation, with NR- TiO_2 /GF presenting the highest C (70 mF). As capacitance is generally proportional to the electrochemically active surface area, this increase suggests that the nanorod architecture provides a substantially larger accessible interface. The constant phase element (CPE) exponent n approached unity for all TiO_2 /GF electrodes, particularly NR- TiO_2 /GF ($n = 0.884$), indicating reduced surface heterogeneity and more ideal capacitive behavior compared to pristine GF [31].

The Bode phase and magnitude plots provided further insight into the interfacial charge-transfer behavior of the electrodes (Fig. 3c,d). In the mid-frequency (MF: $10^2\text{--}10^0\text{ Hz}$) region, a single phase-angle peak corresponding to the charge-transfer process was observed for all electrodes. For the TiO_2 /GF electrodes, this peak shifted to higher frequencies, reflecting faster kinetics and shorter characteristic time constants [30,31]. In contrast, pristine GF exhibited a lower-frequency peak with a smaller phase angle, reflecting sluggish interfacial electron transfer. As shown in Fig. 3d, pristine GF also exhibited the highest low-frequency (LF, $<1\text{ Hz}$) impedance. Among the TiO_2 /GF electrodes,

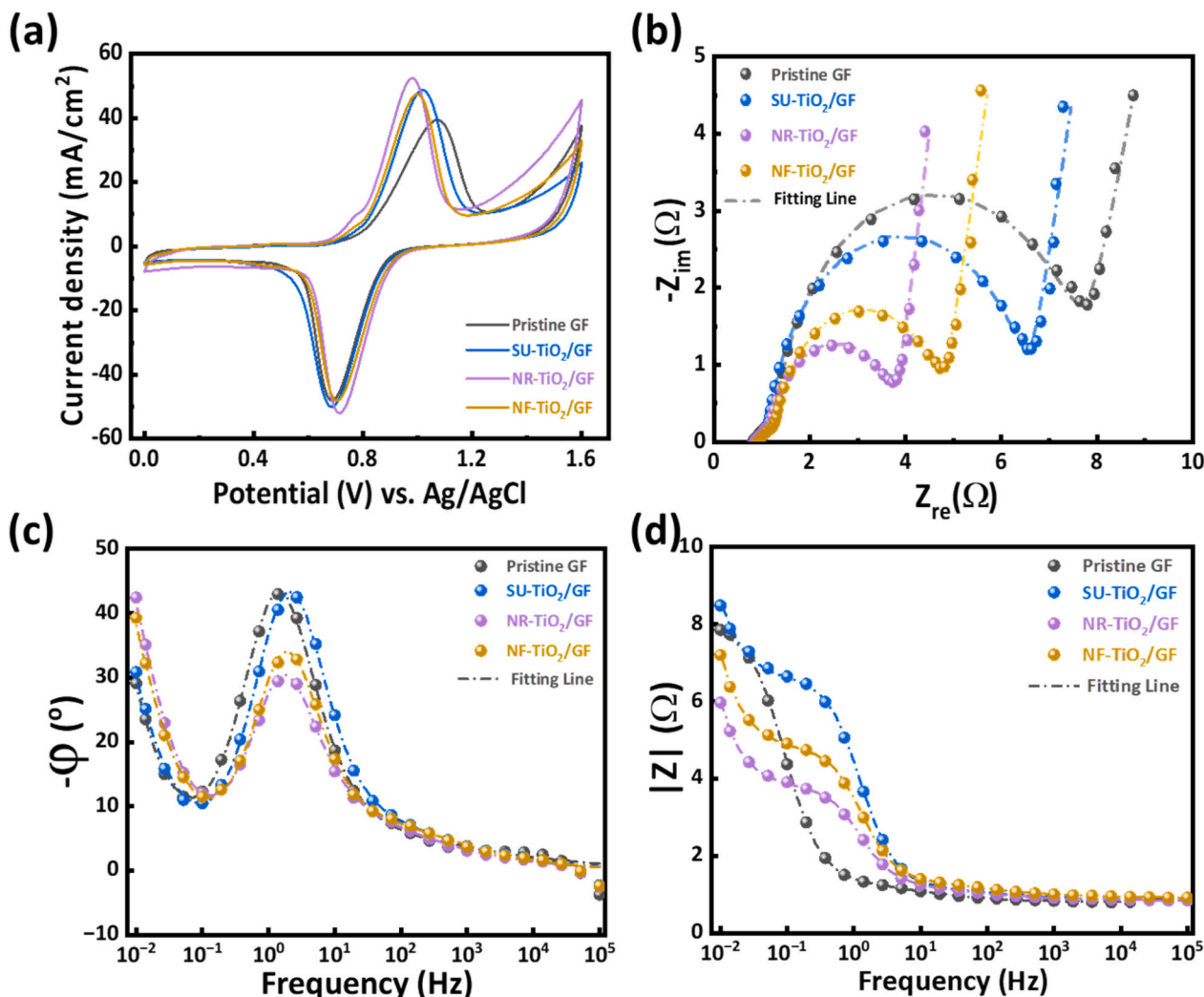


Fig. 3. Electrochemical characterization of pristine graphite felt (GF) and TiO_2/GF electrodes with different nanostructures prepared by in-situ hydrothermal growth: (a) CV curves, (b) Nyquist plots, and Bode plots of (c) phase angle and (d) impedance magnitude obtained from EIS measurements.

Table 1

EIS and CV analysis results of pristine GF and different nanostructures of TiO_2/GF s.

electrodes	EIS					CV					
	R_s (Ω)	R_{ct} (Ω)	C (mF)	Q_{y0}	QN	E_{pa} (V)	E_{pc} (V)	ΔE (mV)	I_{pc} (mA/cm ²)	I_{pa} (mA/cm ²)	I_{pc}/I_{pa}
GF	0.80	6.32	50	2.20	0.83	1.07	0.68	390	39.43	-48.05	0.82
SU- TiO_2/GF	0.83	5.29	34	2.43	0.857	1.01	0.68	330	48.68	-50.06	0.97
NR- TiO_2/GF	0.83	2.39	70.2	2.84	0.884	0.98	0.71	270	52.44	-52.03	1.01
NF- TiO_2/GF	0.91	3.36	47.9	2.35	0.861	1.00	0.70	300	47.44	-48.05	0.98

NR- TiO_2/GF displayed the lowest impedance and the most favorable phase response, consistent with its lower charge-transfer resistance and larger electrochemically accessible interfacial area [32]. While SU- TiO_2/GF and NF- TiO_2/GF also exhibited reduced impedance compared to pristine GF, their responses remained inferior to that of NR- TiO_2/GF , implying less effective suppression of polarization and mass-transfer limitations [33]. Overall, the NR- TiO_2/GF electrode possessed the lowest impedance across the entire frequency range. Taken together, the CV, Nyquist, and Bode analyses consistently demonstrate that TiO_2 nanostructure incorporation substantially enhances the electrochemical functionality of GF, and suggest that the nanorod architecture (NR- TiO_2/GF) provides the most favorable charge-transfer and mass-transport characteristics among the investigated configurations.

3.2. Thermal-Induced Phase and Structural Modulation of NR- TiO_2/GF

To optimize the structural characteristics and electrochemical performance of the NR- TiO_2/GF electrode (prepared at 0.05 M precursor concentration), the effect of post-synthesis calcination temperature (300–600 °C) was systematically investigated.

3.2.1. Morphological evolution and nanorod dimensions

The influence of calcination temperature on the morphology and structural evolution of the optimized NR- TiO_2/GF electrode was investigated by SEM (Fig. S4). Although all samples were synthesized under identical in-situ hydrothermal conditions, the post-synthesis calcination temperature significantly affected the nanorod morphology. At 300 °C,

the NR300-TiO₂/GF retained the high-aspect-ratio nanorod network formed during hydrothermal growth (Fig. S4a). The nanorods remained relatively well separated with open interspaces; however, the relatively low calcination temperature of 300 °C may have resulted in less complete crystallization of the hydrothermally formed nanorods. [34]. Upon increasing the calcination temperature to 400 °C, the NR400-TiO₂/GF developed more defined and compact nanorod bundles with hierarchical subbranches (Fig. S4c). This moderate thermal treatment promoted structural rearrangement and volumetric densification of the preformed amorphous or poorly crystalline segments, while largely preserving the original nanorod architecture. At 500 °C, the NR500-TiO₂/GF electrode exhibited densely distributed and well-defined nanorods with a uniform tree-like hierarchy (Fig. S4e), maintaining its one-dimensional architecture without apparent structural collapse. In contrast, further increasing the temperature to 600 °C induced severe sintering between adjacent nanorods, leading to thick, fused aggregates and partial collapse of the hierarchical structure (Fig. S4g), which is expected to reduce the accessible surface area and hinder electrolyte infiltration [14]. These localized variations in apparent coverage may also reflect minor differences between individual SEM sampling areas rather than a change in total bulk loading. Statistical analysis (Fig. S4) further revealed that the average nanorod diameter was strongly dependent on the calcination temperature. NR400-TiO₂/GF possessed the smallest average effective diameter of 128 nm (Fig. S4d), whereas the diameters for NR300-TiO₂/GF, NR500-TiO₂/GF, and NR600-TiO₂/GF were 159, 251, and 228 nm, respectively (Fig. S4b, f, h). This finer nanorod configuration in NR400-TiO₂/GF is expected to maximize the electrochemically active surface area and shorten ion-diffusion pathways, suggesting that 400 °C provides the most geometrically favorable nanorod architecture.

3.2.2. Thermally driven phase transformation and crystallinity

The influence of calcination temperature on the crystal structure and phase evolution of NR-TiO₂/GF electrodes was examined by XRD (Fig. 4a) and Raman spectroscopy (Fig. 4b). The XRD pattern of NR300-TiO₂/GF exhibited weak TiO₂ diffraction signals, indicating limited crystallization under low-temperature calcination. As the calcination temperature increased, the diffraction peaks became progressively

sharper and more intense, reflecting enhanced crystallinity and structural ordering of the nanostructures [35]. All calcined NR-TiO₂/GF electrodes retain the mixed anatase/rutile phase composition, with characteristic rutile reflections ((110), (101), and (211)) and anatase reflections ((101), (105), and (204)), consistent with JCPDS No. 21-1276 and JCPDS No. 21-1272, respectively [8,25]. The XRD results therefore confirm the temperature-dependent evolution of the mixed-phase TiO₂ structure; however, quantitative determination of the anatase/rutile fractions from XRD is complicated by the overlap between the anatase (101) and GF (002) reflections near 25.3°.

Raman spectroscopy (Fig. 4b) further elucidated the local structural evolution and surface phase composition. For NR300-TiO₂/GF, weak Raman features confirmed incomplete crystallization. At 400 °C, distinct anatase bands (~143 and 395 cm⁻¹) and rutile bands (~234, 443, and 604 cm⁻¹) coexisted [36]. Further increasing the temperature to 500–600 °C significantly strengthened the rutile modes while diminishing the anatase signals, confirming extensive thermally induced transformation from anatase to rutile [37]. Raman peak deconvolution was used to estimate the relative anatase/rutile phase fractions because the anatase (101) and GF (002) reflections overlap in the XRD patterns. The Raman-derived anatase/rutile phase fractions of the NR-TiO₂/GF electrodes at different calcination temperatures are summarized in Table S1. Peak deconvolution (Fig. S5) reveals that NR400-TiO₂/GF preserved a substantial anatase fraction (47.5%), achieving the most balanced anatase/rutile heterojunction interface among the investigated series. Although the numerical phase fractions derived from Raman spectroscopy and XRD slightly differ, owing to their distinct sampling depths and selection rules, both techniques consistently confirm that 400 °C provides an optimal thermal window to establish a well-crystallized mixed-phase architecture while avoiding severe sintering.

3.2.3. Electrochemical performance and charge-transfer kinetics

Static water contact angle measurements (Fig. S6) showed that all NR-TiO₂/GF electrodes exhibited spontaneous wetting regardless of calcination temperature [14]. This indicates that the high hydrophilicity is predominantly governed by the presence of the TiO₂ nanostructure rather than the calcination temperature [38]. Therefore, the differences in electrochemical behavior among the electrodes are primarily

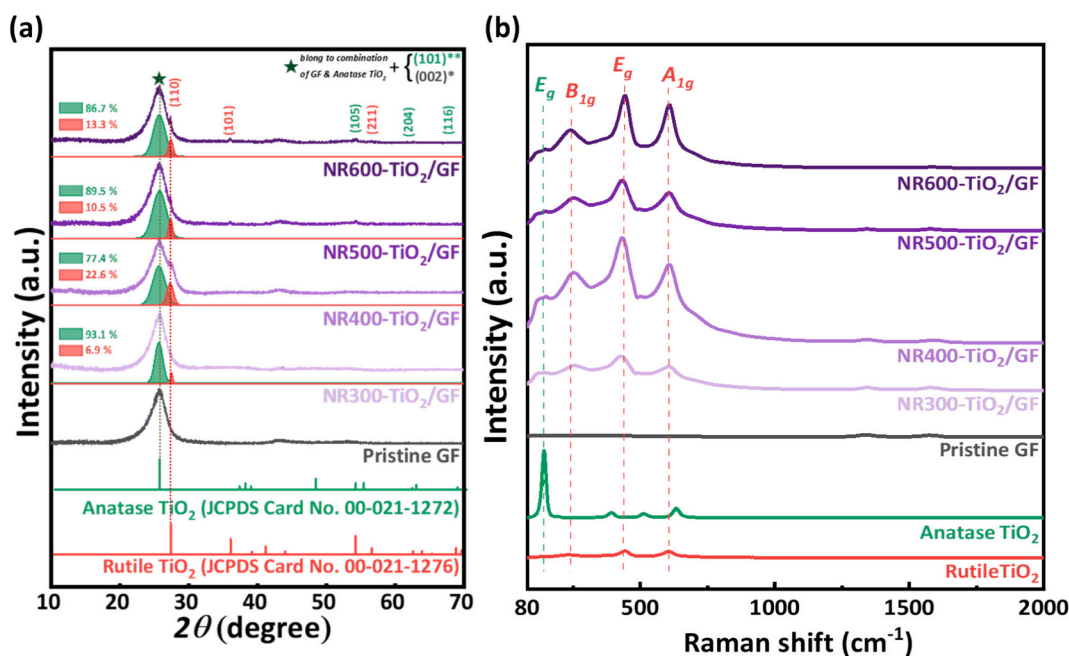


Fig. 4. (a) XRD patterns and (b) Raman spectra of NR-TiO₂/GF electrodes prepared at different calcination temperatures. The NR500-TiO₂/GF sample corresponds to the NR-TiO₂/GF electrode discussed in Section 3.1.

governed by their structural dimensions and phase compositions rather than variations in surface wettability. Subsequently, the electrocatalytic activities of the NR-TiO₂/GF electrodes toward the VO²⁺/VO₂⁺ redox couple were evaluated by CV at 5 mV s⁻¹ (Fig. 5a). All electrodes exhibited distinct redox peaks, with catalytic activities strongly depending on the calcination temperature. As summarized in Table 2, the NR400-TiO₂/GF exhibited the best electrocatalytic performance, achieving the highest peak current densities ($I_{pa} = -55.05 \text{ mA cm}^{-2}$, $I_{pc} = 54.99 \text{ mA cm}^{-2}$) and the smallest ΔE (260 mV), indicating the fastest electron-transfer kinetics and highest redox reversibility. This superior electrochemical performance is primarily attributed to the optimally developed NR-TiO₂ architecture at 400 °C, where a balanced anatase/rutile mixed-phase composition, well-crystallized nanorod network, and fine feature size synergistically provide abundant accessible active sites and continuous charge-transport pathways.

In contrast, electrodes calcined at non-optimal temperatures exhibited reduced activity. At a lower temperature of 300 °C, the incomplete crystallization and lower structural crystallinity of TiO₂ limited electron conduction and redox activity. When the temperature exceeded 400 °C, NR500-TiO₂/GF formed larger nanorods, which is expected to decrease the accessible active surface area. Notably, NR600-TiO₂/GF exhibited severe rod-to-rod fusion and agglomeration; such extensive sintering likely hindered electrolyte infiltration and restricted the exposure of catalytic sites, resulting in electrocatalytic performance

even inferior to that of pristine GF. Consequently, the overall electrochemical activity followed the trend: NR400-TiO₂/GF > NR500-TiO₂/GF > NR300-TiO₂/GF > pristine GF > NR600-TiO₂/GF, consistent with the CV parameters in Table 2.

The temperature-dependent Nyquist plots (Fig. 5b) further confirm these observations. NR400-TiO₂/GF exhibited the lowest R_{ct} at 1.89 Ω , which is substantially lower than the pristine GF value of 6.32 Ω (Table 2), confirming that the refined nanorod architecture and balanced phase structure effectively reduce interfacial kinetic barriers. Correspondingly, the double-layer capacitance, which reflects the electrochemically active surface, reached its maximum at 400 °C and declined at higher calcination temperatures. This trend aligned with the observed structural evolution from well-defined nanorods to larger rods or interconnected agglomerates. Conversely, NR600-TiO₂/GF displayed a significantly elevated R_{ct} of 16.76 Ω . This increase can be attributed to restricted electrolyte accessibility and a reduced active surface area, reinforcing the findings from the SEM observation.

In the Bode phase and magnitude plots (Fig. 5 (c-d)), all electrodes exhibited a distinct MF region phase peak that is associated with interfacial charge-transfer. The NR400-TiO₂/GF electrode displayed the smallest phase angle in the LF region (Fig. 5c) and the lowest overall impedance across the entire frequency range (Fig. 5d). This indicates enhanced ion access and reduced diffusion resistance [39]. Conversely, at higher calcination temperatures, the NR600-TiO₂/GF electrode

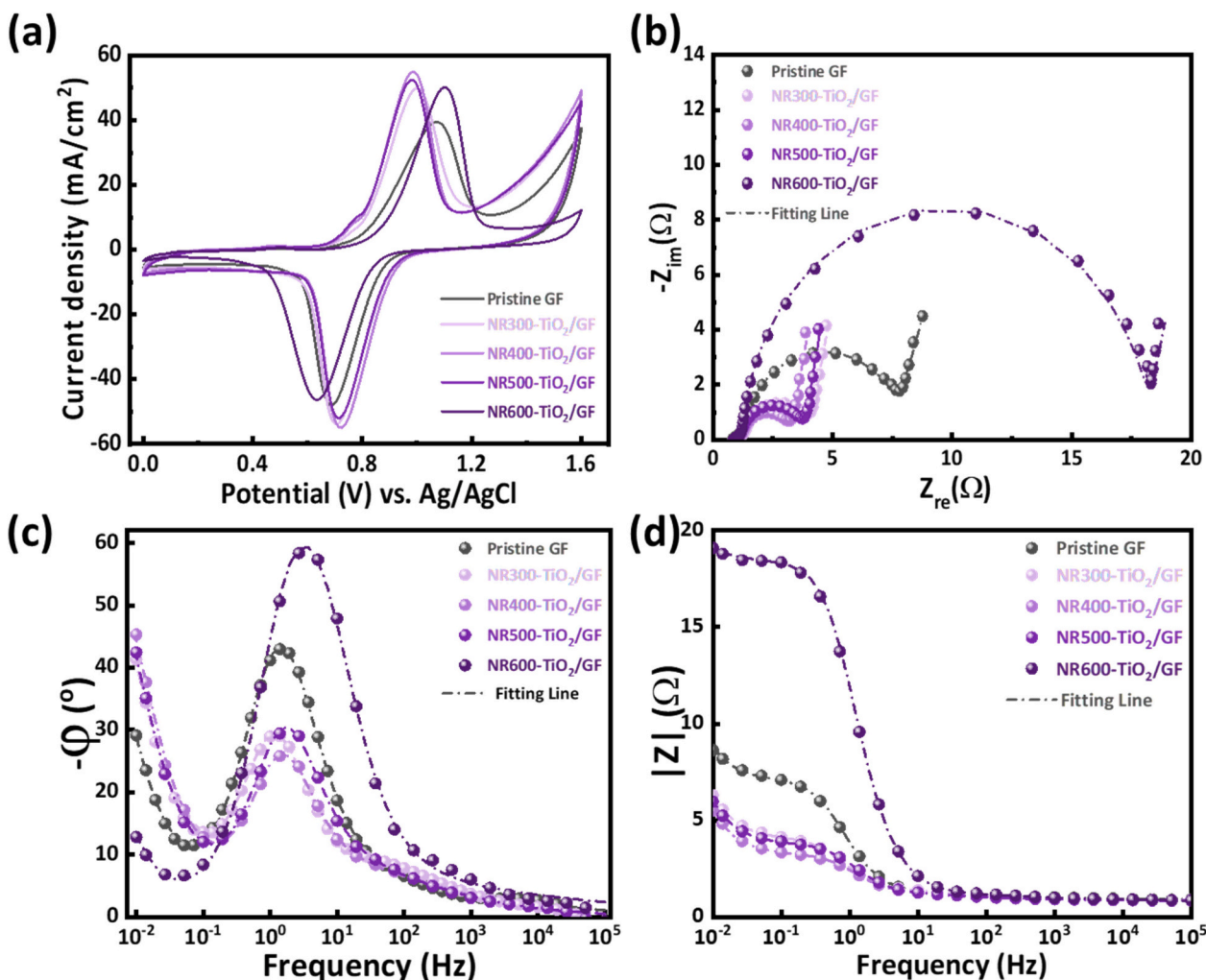


Fig. 5. Electrochemical characterization of pristine graphite felt (GF) and NR-TiO₂/GF electrodes prepared at different calcination temperatures: (a) CV curves, (b) Nyquist plots, and Bode plots of (c) phase angle and (d) impedance magnitude obtained from EIS. (The NR500-TiO₂/GF sample corresponds to the NR-TiO₂/GF electrode discussed in Section 3.1.)

Table 2

EIS and CV analysis results of pristine GF and nanorod TiO₂ decorated graphite felts (NR-TiO₂/GFs) (NR500-TiO₂/GF corresponds to the NR-TiO₂/GF electrode discussed in Section 3.1).

electrodes	EIS					CV					
	Rs (Ω)	Rct (Ω)	C (mF)	Qy0	QN	Epa (V)	Epc (V)	ΔE (mV)	Ipc (mA/cm ²)	Ipa (mA/cm ²)	Ipc /Ipa
GF	0.80	6.32	50	2.20	0.83	1.07	0.68	390	39.43	−48.05	0.82
NR300-TiO ₂ /GF	0.88	2.61	90.2	2.63	0.873	1.00	0.70	300	49.78	−53.84	0.92
NR400-TiO ₂ /GF	0.86	1.89	92.2	2.84	0.877	0.98	0.72	260	54.99	−55.05	0.99
NR500-TiO ₂ /GF	0.83	2.39	70.2	2.84	0.884	0.98	0.71	270	52.44	−52.03	1.01
NR600-TiO ₂ /GF	0.84	16.76	11.2	3.71	0.98	1.10	0.63	470	50.14	−46.34	1.08

showed significantly increased impedance, likely due to severe structural agglomeration that limits electrolyte penetration and diminishes interfacial charge transfer. To further evaluate the electrochemical kinetics of the electrodes, CV measurements were conducted at various scan rates toward the VO²⁺/VO₂⁺ redox couple (Fig. S7a). Both anodic and cathodic peak currents increased with increasing scan rate. A linear relationship between the peak current density and the square root of the scan rate was observed for both electrodes (Fig. S7c), indicating that the VO²⁺/VO₂⁺ redox reaction is predominantly governed by diffusion-controlled processes, according to the Randles-Sevcik relationship. Notably, NR400-TiO₂/GF exhibited a steeper slope than pristine GF, suggesting enhanced electrochemically accessible interfacial area and more efficient mass transport during the redox process. The ratio of anodic to cathodic peak current (I_{pc}/I_{pa}) was further used to evaluate the reversibility of the redox reaction (Fig. S7c). NR400-TiO₂/GF exhibited an I_{pc}/I_{pa} ratio close to unity, reaching 0.99 at a scan rate of 7 mV s^{−1}, indicating improved electrochemical reversibility compared with

pristine GF. Combined with the enhanced Randles-Sevcik response, these results demonstrate that the optimized NR400-TiO₂/GF electrode provides more favorable interfacial redox kinetics toward the VO²⁺/VO₂⁺ redox reaction.

At negative potentials, the hydrogen evolution reaction (HER) typically competes with the V²⁺/V³⁺ redox reaction to induce polarization [10]; therefore, a negative-side CV was performed (Fig. S7d). Compared to pristine GF, NR400-TiO₂/GF exhibited markedly higher redox current densities and lower polarization, indicating improved reaction kinetics and reversibility. The reduced influence of competing side reactions suggested by the CV response may also contribute to the improved negative-side electrochemical behavior. The HER kinetics were further analyzed using Tafel plots (inset of Fig. S7d). NR400-TiO₂/GF exhibited a higher Tafel slope (655 mV dec^{−1}) than pristine GF (570 mV dec^{−1}), indicating less favorable HER kinetics under the investigated conditions. Together with the negative-side CV behavior, these results suggest a reduced contribution of parasitic HER on NR400-TiO₂/GF; however,

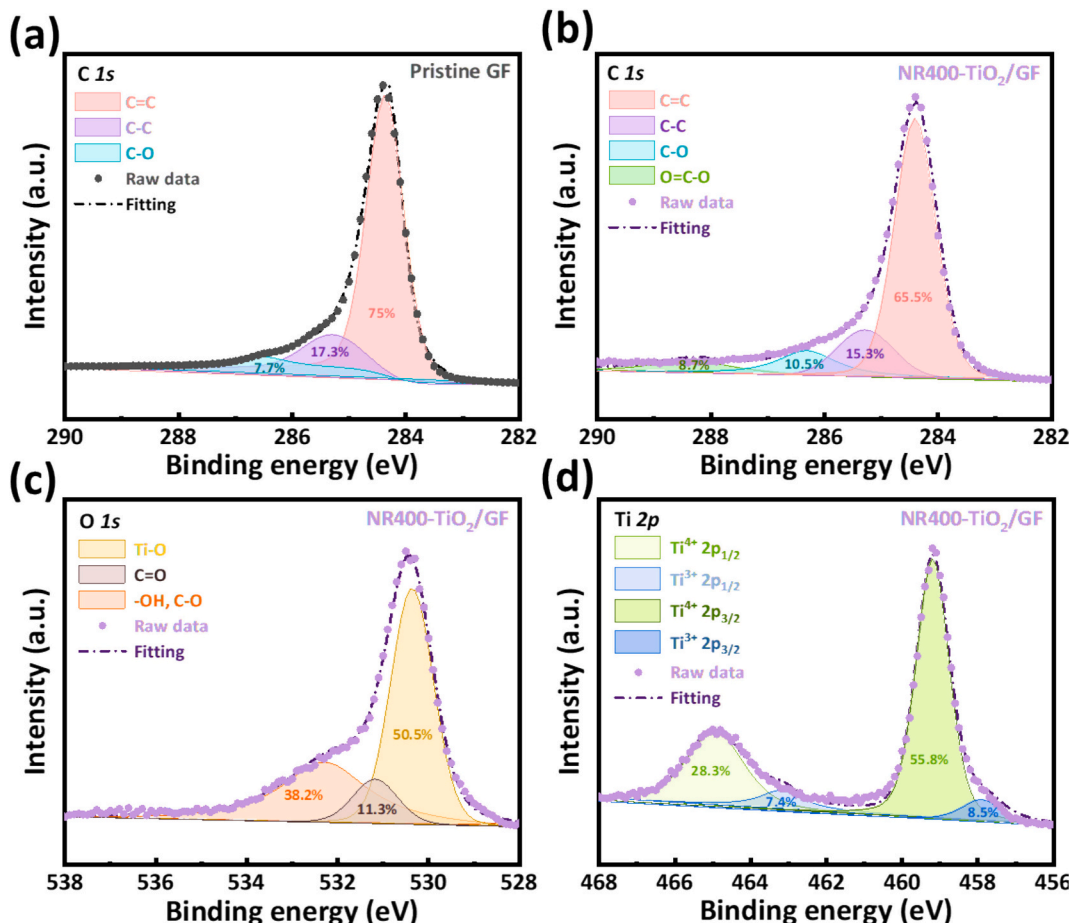


Fig. 6. XPS analysis of pristine GF and NR400-TiO₂/GF electrodes: (a) C 1 s spectrum of pristine GF and (b) C 1 s, (c) O 1 s, and (d) Ti 2p spectra of NR400-TiO₂/GF.

direct HER measurements would be required to quantitatively verify HER suppression. Overall, these kinetic and half-cell evaluations demonstrate that the NR400-TiO₂/GF architecture provides optimal redox activity, minimal interfacial resistance, and efficient mass transport across both half-cell reactions, establishing it as the optimal electrode candidate for subsequent single-cell battery tests.

3.2.4. Surface chemical states and charge-transfer mechanism

To elucidate the microscopic origin of the enhanced electrocatalytic activity and accelerated charge-transfer kinetics in NR400-TiO₂/GF, X-ray photoelectron spectroscopy (XPS) was conducted (Fig. 6). The deconvoluted C 1s spectra of pristine GF (Fig. 6a) exhibit three characteristic components located at approximately 284.4, 285.4, and 286.4 eV, corresponding to C=C (75.0%), C—C (17.3%), and C—O (7.7%), respectively [8,10]. Following the in-situ growth of TiO₂ nanorods (Fig. 6b), the relative proportion of graphitic C=C decreased to 65.5%, accompanied by an increase in oxygen-containing components (C—O at 10.5% and newly emerged O—C=O at 8.7%). These changes suggest an increased contribution of oxygen-containing carbon species within the XPS probing region after the TiO₂ growth process. Such species may originate from the partially exposed GF surface, the TiO₂/GF interfacial region, or surface modifications induced during hydrothermal treatment. The O 1s spectrum of NR400-TiO₂/GF (Fig. 6c) was deconvoluted into three components centered at approximately 530.3, 531.2, and

532.3 eV, which are assigned to lattice Ti—O (11.3%), surface hydroxyl groups (—OH/C—O, 50.5%), and C=O species (38.2%), respectively [9,11].

The prominent concentration of surface hydroxyl groups underscores a highly hydroxylated interface, which facilitates rapid electrolyte penetration throughout the 3D fibrous matrix. The abundant hydroxyl species demonstrate that the TiO₂ nanorods possess a highly hydroxylated surface, which significantly enhances the hydrophilicity of the electrode and promotes rapid electrolyte infiltration throughout the three-dimensional graphite felt network. Furthermore, the Ti 2p spectrum (Fig. 6d) displays predominant peaks at 458.8 eV (Ti⁴⁺ 2p_{3/2}) and 464.5 eV (Ti⁴⁺ 2p_{1/2}), confirming the formation of TiO₂. Deconvolution also revealed minor components assigned to Ti³⁺ 2p_{3/2} and Ti³⁺ 2p_{1/2}. The coexistence of mixed Ti³⁺/Ti⁴⁺ valence states suggest the presence of oxygen vacancies induced during thermal processing, which can serve as shallow donor states to enhance electronic conductivity and promote interfacial charge transfer during vanadium redox processes [8,11].

These surface chemical features are closely aligned with the electrochemical double-layer capacitance (C_{dl}) measurements in 2 M H₂SO₄ [10]. The calculated C_{dl} increased significantly from 54.7 mF for pristine GF to 87.5 mF for NR400-TiO₂/GF (an ~60% enhancement), corresponding to an approximately 60% enhancement, quantitatively demonstrating that the hierarchical nanorod architecture exposes significantly more electrochemically accessible active interfaces.

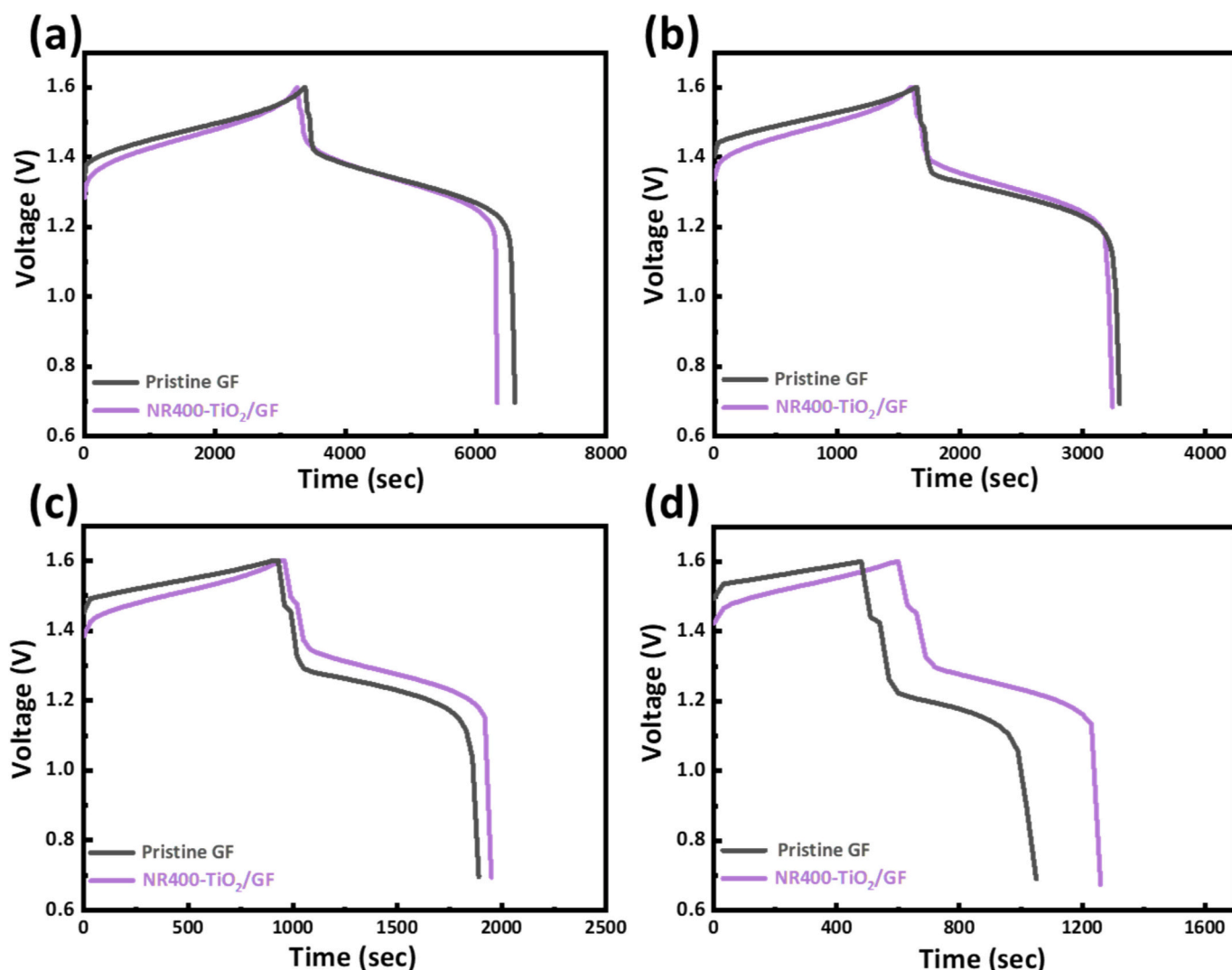


Fig. 7. Charge-discharge curves of pristine graphite felt (GF) and NR400-TiO₂/GF electrodes at current densities of (a) 40, (b) 60, (c) 80, and (d) 100 mA cm⁻².

Collectively, the synergistic integration of an enlarged active surface area, abundant surface hydroxyl groups, and an oxygen-vacancy-rich mixed-phase TiO_2 interface accounts for the superior reaction kinetics and durability of the NR400- TiO_2 /GF electrode.

3.2.5. Single-cell VRFB performance

To validate the practical feasibility of the optimized electrode, NR400- TiO_2 /GF was integrated as both the positive and negative electrodes in a full-cell VRFB configuration. Fig. 7 compares the charge-discharge profiles of NR400- TiO_2 /GF and pristine GF across various current densities ($40\text{--}100\text{ mA cm}^{-2}$) within a voltage window of $0.6\text{--}1.6\text{ V}$. At low current densities (40 and 60 mA cm^{-2}), both electrodes exhibited comparable profile shapes and discharge capacities, indicating modest kinetic resistance under mild operating regimes. However, as the current density increases to 80 and 100 mA cm^{-2} , the NR400- TiO_2 /GF electrode delivered markedly longer charge-discharge durations and higher capacity retention than pristine GF. Specifically, NR400- TiO_2 /GF maintained discharge durations of 3256 , 1610 , 955 , and 600 s at 40 , 60 , 80 , and 100 mA cm^{-2} , respectively. This markedly suppressed voltage polarization and superior rate capability directly stem from the well-crystallized, mixed-phase (anatase/rutile) vertically

aligned TiO_2 nanorods, which mitigate transport resistance, provide abundant accessible catalytic sites, and accelerate interfacial redox kinetics as established in the CV and EIS analyses [40].

Fig. 8(a–c) summarizes the energy efficiency (EE), coulombic efficiency (CE), and voltage efficiency (VE) as functions of current density (Table S2). The CE values of both electrodes remained nearly identical across the entire current-density range, indicating that the introduction of the TiO_2 nanorod architecture did not adversely affect the charge-discharge efficiency of the VRFB. In contrast, NR400- TiO_2 /GF consistently outperformed pristine GF in VE across all testing rates, with the enhancement becoming increasingly prominent at high current densities. Notably, at 140 mA cm^{-2} , the VE rose from 69.5% for pristine GF to 80.3% for NR400- TiO_2 /GF, directly reflecting reduced ohmic and charge-transfer overpotentials. Consequently, the improved VE translated into superior EE values; at 80 and 100 mA cm^{-2} , NR400- TiO_2 /GF achieved EEs of 85.8% and 83.7% , representing absolute enhancements of 9.9% and 11.4% over pristine GF, respectively. To further benchmark the cell performance, Fig. 8d compares the rate-dependent EE of NR400- TiO_2 /GF with previously reported metal-oxide-modified graphite felt electrodes (detailed cell configurations and electrochemical parameters are summarized in Table S3). Notably, the NR400- TiO_2 /GF electrode

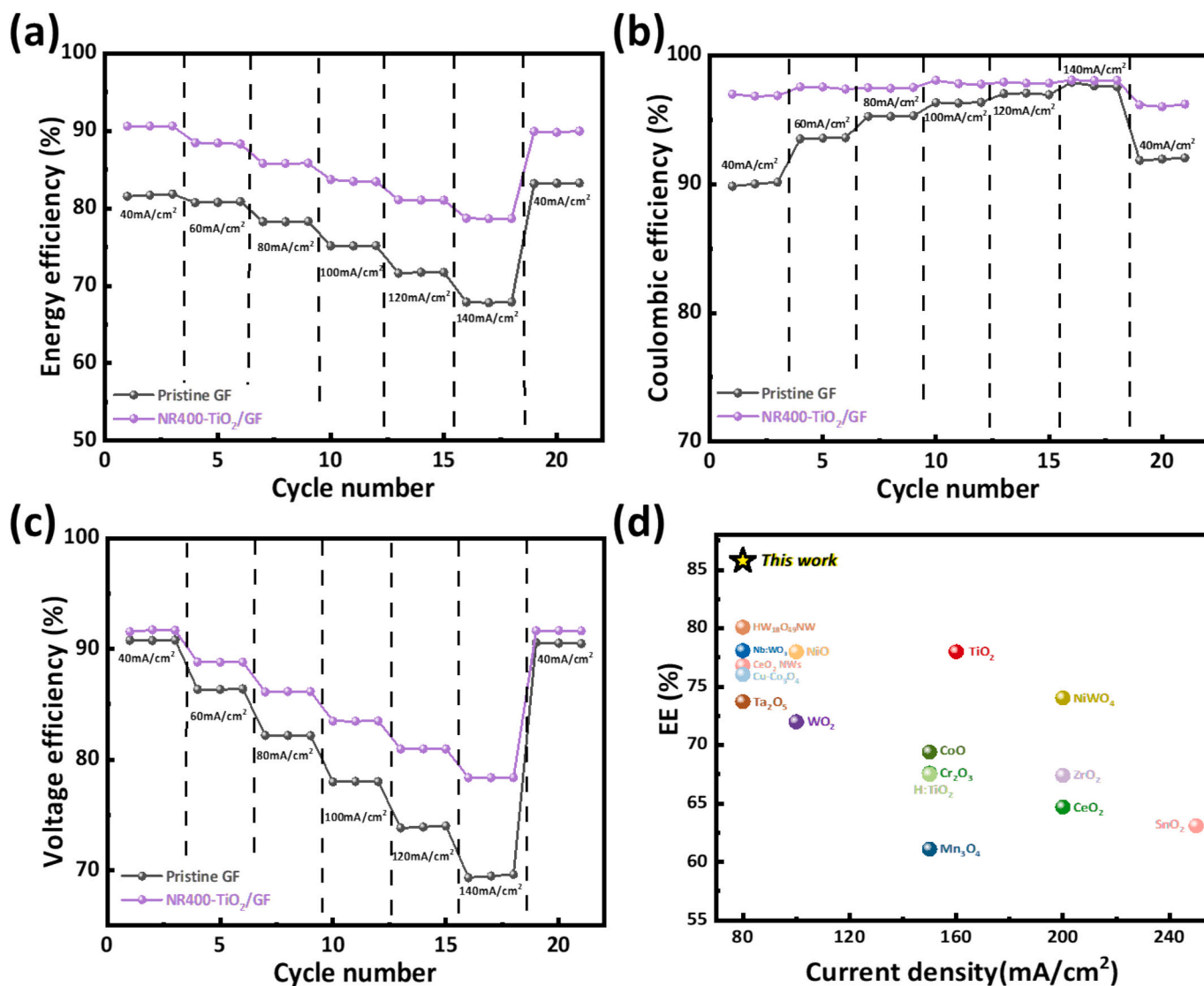


Fig. 8. Electrochemical performance of pristine graphite felt (GF) and NR400- TiO_2 /GF electrodes: (a) energy efficiency (EE), (b) coulombic efficiency (CE), and (c) voltage efficiency (VE) at different current densities; and (d) comparison of the EE values of metal oxide-modified graphite felt electrodes for VRFBs reported in the literature.

exhibited higher energy efficiency across all evaluated current densities, outperforming representative metal-oxide systems reported to date. The superior performance of NR400-TiO₂/GF is primarily attributed to the unique electronic and catalytic synergy of its well-balanced anatase/rutile mixed-phase nanorod architecture. Specifically, the staggered band alignment between the coexisting anatase and rutile phases establishes an intimate heterojunction interface with a built-in energy offset, which significantly expedites interfacial electron transfer and reduces charge-transfer barriers. Furthermore, the localized lattice mismatch at the phase boundaries introduces abundant surface defects and oxygen vacancies, serving as highly active catalytic centers for vanadium redox couples (V^{2+}/V^{3+} and VO^{2+}/VO_2^+). Coupled with the one-dimensional vertically aligned nanorod configuration that facilitates electrolyte percolation and mass transport, this mixed-phase heterostructure effectively suppresses kinetic polarization and ensures robust interfacial durability during high-rate battery cycling [41].

3.2.6. Post-cycling structural and interfacial stability

To evaluate long-term durability, continuous charge-discharge cycling was conducted at a current density of 80 mA cm⁻² (Fig. S8) for 800 cycles. The NR400-TiO₂/GF electrode exhibited outstanding cycling stability and sustained energy efficiency, whereas pristine GF suffered progressive efficiency deterioration and capacity decay. The NR400-TiO₂/GF electrode maintains an average energy efficiency above 80% throughout the test, demonstrating excellent long-term durability. In contrast, the pristine GF exhibits rapid performance degradation and fails before 400 cycles. VRFB durability test during the 800 cycles at the same current density by EE, CE, and VE is also shown in the inset of Fig. S8. Post-mortem SEM images (Fig. S9) directly account for this divergence. Pristine GF exhibited severe oxidative etching pits and longitudinal grooves on the carbon fibers (Fig. S9a), whereas NR400-TiO₂/GF preserved its structural integrity with dense, intact TiO₂ nanorod arrays firmly anchored on the fibers (Fig. S9b), demonstrating effective physical shielding against electrolyte corrosion [39,42]. Post-cycling XPS analysis (Fig. S10) further confirmed the interfacial chemical resilience of NR400-TiO₂/GF, wherein surface -OH groups, lattice Ti—O bonds, and Ti³⁺ defect states were largely retained with negligible degradation. Consequently, NR400-TiO₂/GF maintained a high electrochemical double-layer capacitance of 83.2 mF after cycling, substantially higher than that of cycled pristine GF (25.1 mF). Collectively, these post-cycling evaluations confirm that the TiO₂

nanorod architecture synergistically mitigates carbon fiber erosion, preserves electrocatalytic defect sites, and ensures superior long-term durability for VRFB applications.

3.2.7. Proposed electrocatalytic mechanisms

Based on the systematic physicochemical, electrochemical, and post-mortem characterizations, a comprehensive catalytic and protective mechanism for the NR400-TiO₂/GF electrode is proposed (Fig. 9). The superior performance across both half-cells is predominantly governed by the unique synergy between the mixed-phase anatase/rutile heterojunction, abundant surface defect states, and the one-dimensional nanorod architecture. In the positive half-cell, the intrinsically sluggish VO^{2+}/VO_2^+ redox reaction proceeds via a proton-coupled electron transfer (PCET) pathway involving multi-step oxygen transfer; here, the phase-boundary lattice mismatch generates abundant oxygen vacancies (V_o) that, together with surface hydroxyl groups, drastically lower the activation barrier for H₂O coordination and O—H bond cleavage [42,43]. The phase composition and nanostructured architecture of TiO₂ can further influence its charge-transport behavior and electrochemical response [34,44,45]. Concurrently, previous studies of anatase/rutile TiO₂ heterostructures have reported staggered band alignment and interfacial charge-transfer behavior [18,19,46–48]. Accordingly, the anatase/rutile interface in NR400-TiO₂/GF may facilitate interfacial charge redistribution and charge transfer, contributing to the enhanced electrochemical behavior observed in this study [49,50]. In the negative half-cell, the Ti³⁺/V_o defect sites provide favorable coordination environments for hydrated V³⁺ adsorption and desolvation, facilitating single-electron transfer, while the dense TiO₂ nanorod sheath physically isolates carbon active sites, thereby elevating the overpotential for the parasitic hydrogen evolution reaction (HER) [47,51]. The TiO₂ nanorod layer may also modify the electrode/electrolyte interface and reduce the contribution of competing side reactions, including HER, as suggested by the negative-side CV behavior [12,34]. Furthermore, the thermodynamically robust rutile scaffold and the vertically aligned nanorod arrays serve as an effective protective shield, preventing direct acidic and oxidative etching of the carbon substrate [52,53]. Unlike single-phase anatase or rutile, which involve a trade-off between catalytic activity and structural stability, the mixed-phase anatase/rutile heterojunction integrates these complementary properties while promoting interfacial defect formation and charge redistribution [45,54]. Consequently, the optimized NR400-TiO₂/GF architecture simultaneously accelerates

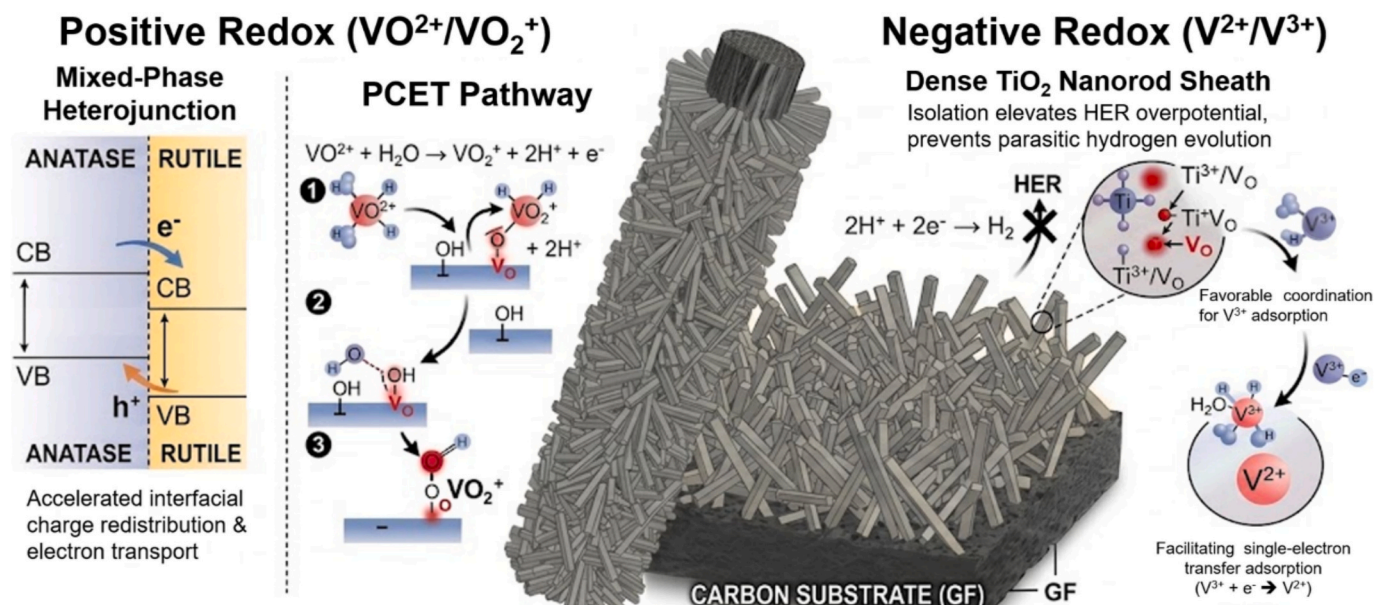


Fig. 9. Schematic illustration of the proposed electrochemical enhancement mechanism of the NR400-TiO₂/GF electrode.

redox kinetics, suppresses parasitic side reactions, and prevents structural degradation, delivering exceptional rate capability and long-term durability in VRFBs.

4. Conclusion

In summary, hierarchical TiO₂/GF electrodes were successfully fabricated via a concentration- and temperature-driven dual-modulation strategy based on the direct in-situ hydrothermal growth of TiO₂ nanostructures. By precisely regulating the precursor concentration during in-situ heterogeneous nucleation and anisotropic growth, vertically aligned one-dimensional TiO₂ nanorods (NR-TiO₂/GF) firmly anchored onto the carbon fibers were identified as the optimal morphological configuration, providing seamless conductive interfaces, continuous electron-transport pathways, and unobstructed channels for rapid electrolyte percolation.

Subsequent modulation of the post-calcination temperature revealed that annealing at 400 °C (NR400-TiO₂/GF) achieved an optimal synergy among nanorod dimensions (average diameter of ~128 nm), crystallinity, and phase composition. The in situ-formed, well-balanced anatase/rutile heterojunction interface, coupled with abundant surface hydroxyl groups and intrinsic oxygen vacancies, significantly expedited interfacial charge redistribution and lowered charge-transfer activation barriers without requiring chemical reduction post-treatments or conductive additives.

Electrochemical evaluations demonstrated that NR400-TiO₂/GF exhibited the lowest charge-transfer resistance ($R_{ct} = 1.89 \Omega$), minimal polarization, and accelerated mass transport across both positive (VO²⁺/VO₂⁺) and negative (V²⁺/V³⁺) half-cell reactions. When integrated into a full-cell VRFB, the NR400-TiO₂/GF electrode delivered energy efficiencies of 85.8% at 80 mA cm⁻² and 83.7% at 100 mA cm⁻², outperforming pristine GF and benchmark metal-oxide modifications. Furthermore, post-mortem analyses confirmed that the robust, in-situ grown TiO₂ nanorod sheath effectively shielded the underlying carbon substrate against oxidative corrosion and suppressed parasitic hydrogen evolution, ensuring outstanding structural and electrochemical durability during extended cycling. This work demonstrates a facile and potentially scalable in-situ synthesis strategy for designing low-dimensional mixed-phase metal oxide electrocatalysts for high-performance and long-life energy storage systems.

CRedit authorship contribution statement

Iqra Shaheen: Writing – review & editing, Writing – original draft, Methodology. **Shih-Hsuan Chen:** Writing – review & editing, Software. **Yu-Xian Lee:** Software. **Wei-Hao Chiu:** Resources. **Ting-Han Lin:** Software, Resources. **Kumar GokulKumar:** Writing – review & editing, Software. **P. Varatharajan:** Writing – review & editing, Software. **Jen-Fu Hsu:** Resources. **Gao Chen:** Writing – review & editing, Resources. **Kun-Mu Lee:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Funding acquisition.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.183177>.

Data availability

Data will be made available on request.

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