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Specific capacitance ($F_{g}^{-1}$) vs. scan rate (mVs$^{-1}$)

- W70
- W90
- W110

Temperatures: 70°C, 90°C, 110°C

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Morphology and crystal structure dependent pseudocapacitor performance of hydrated WO$_3$ nanostructures

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Abstract

The strategic morphology tuning of hydrated WO$_3$ nanostructures from the two-dimensional (2D) nanosheets to three-dimensional (3D) slabs with enhanced in-plane crystalline nature and multilayered construction are realized via tailoring synthesis temperatures. The increasing synthesis temperature expands the degree of crystallinity, specific surface area and thickness of layered WO$_3$H$_2$O sheets that result into slab like 3D morphology characterized by X-ray diffraction spectra (XRD), Raman spectra and scanning electron microscopy (SEM). The electrochemical study reveals the higher specific capacitance 386 Fg$^{-1}$ of 3D slabs than 2D nanosheets (254 Fg$^{-1}$) at scan rate 2 mVs$^{-1}$. Moreover, the 3D slab demonstrates the excellence capacitance retention of 96% than 2D nanosheets of 86% after 3000 cycles. The enhanced performance of supercapacitor in 3D slabs is attributed to three significant aspects, first confined coordinated hydrate into the crystalline layer enables significant surface area and the fast electrochemical proton insertion via Eigen-Zundel-Eigen mechanism, secondly the enhanced crystalline nature offers improved in-plane conductivity and finally the structural defects and disorders employed by the layered structure promote the faradic redox reactions.

Keywords

Intercalation; layered structure; crystallinity; transition metal oxide; capacitance.
1. Introduction

The energy scenario at the global level is on insisting efficient efforts towards green and clean energy to fulfill the enormous demand of future generations. In this context, different energy harvesting related activities are initiated and implemented through renewable energy resources, however, the energy storage at a large scale is still challenging. The highly efficient and next-generation energy storage devices are required to fulfill the desire of the smart civilization, for example long-lasting portable electronic devices, ecofriendly e-vehicles and so on.¹⁻⁴ Both batteries and supercapacitors are promising electrochemical energy storage devices. Remarkably, the supercapacitors ensure fascinating properties such as fast charging-discharging rate, millions of life cycles and high power density than batteries.⁵⁻⁶ Nevertheless, the supercapacitor has a limitation in practical application because of its low energy density.⁷⁻⁸ The charge storage mechanisms distinguish the supercapacitors into two categories, electrical double layer capacitor (EDLC) and pseudocapacitor.⁹⁻¹⁰ The carbon electrodes exhibit EDLC owing to physically absorbing the charges on a higher surface area without faradic reaction at the interface between the electrode-electrolyte.¹¹⁻¹² Whereas, the B.E Conway has defined the pseudocapacitor that arises due to three process; 1) under potential deposition above the redox potential, the metal ions or proton adsorb on a metal surface, 2) redox capacitor, arises due to faradic redox on the surface or near the surface of electrode materials and 3) intercalated pseudocapacitor, fast faradic insertion of ions into the tunnel or inter-layers of electrode material.¹³⁻¹⁴ The pseudocapacitor type electrodes are highly demanded as a consequence of its capability to boost the energy density of supercapacitors with marginally compromising power density and cyclic life.¹⁵

Usually, the transition metal oxides (TMO) such as RuO₂, MnO₂, NiO, Co₃O₄ emphasizes the pseudocapacitive charge storage mechanism and prominently employed as a cathode material
in the supercapacitors.\textsuperscript{16-20} The cathode materials are suffering from high cost, toxicity, low density and low conductivity for practical application.\textsuperscript{21-22} Recently, more attention has been devoted to WO\textsubscript{3} structure owing to the three-dimensional (3D) lattice network similar to perovskite unit, which consists of corner and edge sharing of octahedral (WO\textsubscript{6}).\textsuperscript{23-24} However, it’s a cost-effective and has excellent physical and chemical properties such as n-type wide band gap, high density (7.13 g cm\textsuperscript{-3}), various oxidation states (W\textsuperscript{+2}-W\textsuperscript{+6}), variable electrical conductivity (10\textsuperscript{-10}-10\textsuperscript{-6} S cm\textsuperscript{-1}).\textsuperscript{25-26} Also, WO\textsubscript{3} exists various crystalline phase which makes the WO\textsubscript{3} as an extraordinary material amongst the other TMO for electrochromic, photocatalytic, gas sensing and electrochemical energy storage application.\textsuperscript{27-31} Moreover, the various crystal phase including trigonal tunnel and cavities are greatly favorable for tuning its physical properties and electrochemical ion intercalation.\textsuperscript{32-35} Interestingly, the hydrated form of WO\textsubscript{3} such as WO\textsubscript{3}nH\textsubscript{2}O (n=2, 1, 0.5, 0.33) exhibits two-dimensional (2D) infinite layered crystal structure as a result of the confined water into the crystalline structure.\textsuperscript{36} The crystal structure can be tuned by confined hydrate, for example, the monohydrate WO\textsubscript{3}H\textsubscript{2}O is a distorted structure composed of two-dimensional crystal structures with appropriate van der Waal gaps between the stacks.\textsuperscript{37,38} The layer of octahedral (WO\textsubscript{6}) composed of four equatorial oxygen atom to form bridging O-W-O bond along the ab-plane. Another axial has occupied by the co-ordinate hydrate (W-OH\textsubscript{2}) bonds and opposite axial is bounded by terminal oxygen atom (W=O) perpendicular to sheets (along c-axis). It is impossible to build W bond with adjacent layers by structural hydrate arrangement and possess the infinite 2D layered structure.\textsuperscript{39} These coordinated water molecules maintain the Eigen-Zundel-Eigen mechanism of rapid proton conduction as in the bulk water and improved the ions storage accessibility owing to 2D layered structure.\textsuperscript{40} Kumagai et al. demonstrated the hydrated H\textsubscript{2}WO\textsubscript{4} of capacity 450 Ah kg\textsuperscript{-1} is much higher than anhydrous WO\textsubscript{3}.
(180 Ah kg\(^{-1}\)), but did not report the energy storage kinetics.\(^{41}\) Recently, Mitchell et al. have confirmed structural water within the crystalline layers that provided the rapid proton transfer kinetics.\(^{42}\) Whereas, the surface redox chemistry via terminal oxygen atom and diffusion of a proton within the hydrogen bond network of confined water layers in MXene hydrate has offered suitable faradic reactions.\(^{43}\) Accordingly, the electrochemical charge storage mechanisms of electrode material are highly subjective to its morphology, electrical conductivity and crystalline nature.\(^{44,45}\) The 2D layered crystalline MoO\(_3\), Nb\(_2\)O\(_5\), V\(_2\)O\(_5\), anatase TiO\(_2\), \(\delta\)-MnO\(_2\) with porous nature have demonstrated the high-rate charge storage capability via intercalation pseudocapacitor mechanism.\(^{46-51}\)

In this study, we proposed the facile strategy for the synthesis of single crystalline and confined hydrate into the 2D layered crystal structure of WO\(_3\) nanostructure for supercapacitor applications. The obtained 3D WO\(_3\) slabs at synthesis temperature 110 °C are succeeding the highest degree of crystallinity and strong bond strength than 2D WO\(_3\) sheets prepared at 70 °C and 90 °C. The morphology and crystal structure dependent electrochemical charge storage performance of 3D slabs and 2D nanosheets were investigated. Further, the proton insertion into the layered crystalline structure i.e. a signal of intercalated pseudocapacitance was confirmed.

2. Materials and methods

2.1. Material and reagent

Sodium tungstate dihydrate (Na\(_2\)WO\(_4\)2H\(_2\)O), concentrated sulfuric acid (H\(_2\)SO\(_4\)) and ethanol were purchase from SD fine, Whatman paper was purchased from Sigma Aldrich. All the aqueous solutions were prepared from the double distill water (DDW) unit.

2.2. Synthesis of hydrated WO\(_3\) nanosheets
The hydrated WO$_3$H$_2$O nanosheets were prepared by one step wet chemical method without addition of surfactant and varying the pH of the solution. The sodium tungstate (500 mg) was slowly added into the 100 ml of aqueous 1M H$_2$SO$_4$ solutions, followed by stirring at room temperature for 30 min. After stirring at room temperature, the above solution was further heated at temperature 70 °C for 1 h. After this, the solution was naturally cooled down to room temperature and washed with continuous DDW and ethanol. The obtained product was dried at 80 °C for 12 h.

For the synthesis of hydrated WO$_3$H$_2$O slabs, the reaction was carried out at higher temperatures 90 °C and 110 °C respectively, keeping the other synthesis parameter same. The obtained final product at synthesis temperature 70 °C, 90 °C and 110 °C were named W70, W90 and W110 respectively.

2.3. Materials characterization

The crystal structure, phase purity and microstructure were characterized by X-ray diffractometer (XRD) of λ= 1.54056 Å with CuKα radiation (Bruker D2 phasor) and Raman Microscope Model (RENNISHAW inVia). The weight loss in a sample was measured by thermogravimetric analysis with a TA 2000 thermoanalyzer. The morphological investigation was done by field emission scanning electron microscopy (FESEM) (FEG Inspect 50, FEI) and (HR-TEM) high-resolution transmission electron microscopy with (SAED) selected area electron diffraction, (TECNAI G2-20-TWIN TEM) operating at 300 kV. The chemical composition and various oxidation states were investigated by XPS (Al-Kα source, PHI 5000 Versa probe scanning ESCA microprobe).

2.4. Electrochemical measurement

The electrochemical measurements were carried out in an Autolab PGSTAT 302N system using a three-electrode assembly. The glassy carbon was used as a working electrode, platinum wire
and Hg/HgCl electrode were used as counter and reference electrode respectively. The active mass of 5 mg was dispersed in 2 ml of water-ethanol solvent of ratio 1:1, 20 µl of Nafion were used as a binder and further, sonicated for 5 min. The 10 µl of homogenous ink was loaded on a polished working electrode and dried under the IR lamp for 30 min. The aqueous 1M H₂SO₄ solutions were used as an electrolyte for all electrochemical measurements. The following equations were used to calculate the specific capacitances from the CV and GCD curves.

\[ C = \frac{\int I dV}{mV(V_b - V_a)} \]  
\[ C = \frac{I \Delta t}{m \Delta V} \]

Where, C is specific capacitance, I/m is current density; \( \Delta t \) and \( \Delta V \) are discharge time and operating voltage window respectively.

3. Results and discussion

3.1. Structural and morphological investigations of hydrated WO₃ nanoslabs

The three hydrated WO₃ nanostructures namely W70, W90 and W110 were synthesized at three different temperatures 70 °C, 90 °C and 110 °C respectively. The crystal structure and purity of hydrated WO₃ nanostructures (W70, W90 and W110) were examined by XRD and Raman spectra (Fig. 1). The XRD pattern (Fig. 1(a)) clearly exhibits the monohydrate orthorhombic crystal structure of tungsten oxide (o-WO₃·H₂O) (JCPDS: 01:084:0886) with lattice parameter \( a=5.24, b=10.71, c=5.133 \) of space group Pmn̅b (62) at all temperatures. However, the sample-W110 depicts the most intense diffraction (111) plane (inset of Fig. 1(a)) which reflecting the higher crystalline structure than the samples W70 and W90. Furthermore, the crystalline size (D)
of W70, W90 and W110 were investigated by Scherrer equation as followed:

\[
D = \frac{0.94 \times \lambda}{\beta \cos \theta}
\]

(3)

Where, \( \lambda \) is 1.54056 Å and 0.94 is constant for CuK\( \alpha \) radiation, \( \beta \) is line broadening in radian (FWHM). The estimated crystalline sizes along the plane (111) are 35 nm to 42 nm and 51 nm of sample W70, W90 and W110 respectively. Fig. 1(b) represents the schematic of the crystal structure of \( \text{o-WO}_3 \text{H}_2 \text{O} \). This structure clearly emphasizes the layer structure of the octahedral (\( \text{WO}_6 \)) along the ab-plane. The four oxygen atoms are coordinated with central W atom forming O-W-O bridge along ab-plane, other open axial is bonded by terminal oxygen atom (W=O) perpendicular to ab-plane and opposite site is co-ordinate by a hydroxyl group (W-OH\( _2 \)) in c-axis. Therefore it’s difficult to create bonding between adjacent layers to form a 2D infinite layered crystalline structure. The Raman spectra (Fig. 1(c)) was investigated to further evaluate the various crystalline symmetry and microstructure of sample W70, W90 and W110. The Raman spectra of the sample W110 illustrates the highly intense band at 645 cm\(^{-1}\) and 946 cm\(^{-1}\) than sample W90 and W70 which reveals the strong bond characteristics feature in sample W110. The band at 946 cm\(^{-1}\) corresponds to the terminal W=O bond that arises due to the confined hydrate between the layered structure. The broad peak in a range of 500-700 cm\(^{-1}\) illustrates the stretching mode of bridging O-W-O bond in ab-plane, as expected from the 2D structure of the \( \text{WO}_3 \text{H}_2 \text{O} \) network. The translational motion of hydrogen atom in octahedral \( \text{WO}_5 \text{OH}_2 \) was assigned to a band at 370 cm\(^{-1}\). The band below 200 cm\(^{-1}\) corresponds to the lattice mode.\(^{53}\) The TGA curve (Fig. 1(d)) confirms the weight loss of coordinated water molecules around temperature 200 °C as agreed with previously reported temperature and approving the monohydrate \( \text{WO}_3 \) structure.\(^{54}\)

The synthesis temperature has a tremendous impact on morphological and structural
change owing to the growth kinetics without alteration of pH and the addition of surfactant. The morphological analysis of sample W70, W90 and W110 were performed by FESEM (Fig. 2). The low-resolution image of W70 (Fig. 2(a)) shows a bunch of nanosheets like architecture. Furthermore, the high-resolution FESEM images (Fig. 2(b)) show the average thickness of a sheet is in the range of 30-40 nm. Further, increasing the synthesis temperature to 90 °C (W90) the thickness of the nanosheets increases to 60-100 nm as shown in Fig. 2(c) and 2(d). Moreover, at high synthesis temperature 110 °C, the densely packed 3D slab like morphology is created (Fig. 2(e)) and the high resolution FESEM image (Fig. 2(f)) displays the thickness of slabs increases to 200-250 nm. These slabs are made up of attachment of 4-5 nanosheets together along the surface side and expose the top edges open. Furthermore, the low-magnification TEM image of sample W110 (Fig. 3(a)) illustrates the fragmented sheets affected by sonication. The HRTEM image (Fig. 3(b)) exhibits the interplanar spacing of 0.345 nm which corresponds to d-spacing of (111) plane. The inverse fast Fourier transform (IFFT) images (Fig. 3(c)) of the selected region of Fig. 3(b) signifies the various defects such as frank disorder and stacking fault. These defects have a strong impact on stress and electrostatic repulsion between the layers, which can directly alter the migration energy, diffusion barriers, and proton or alkali ion must overcome during intercalation. Fig. 3(d) represents the intensity profile of Fig. 3(c). The SAED pattern (Fig. 3(e)) illustrates the set of bright diffraction spots indicating the single crystalline nature of sample W110 and the SAED pattern can be an index to the (001) zone axis of orthorhombic WO$_3$H$_2$O. It is also observed that, along with the strong electron diffraction spot such as (111), the weak diffraction spots can also be noted at those forbidden sites which is indicated by a white arrow. These weak spots are assigned to diffraction from the higher order Laue zone due to the combination of elongation of diffraction spot along the normal of slabs and
the larger (001) atomic spacing.

The chemical composition and various oxidation states of WO$_3$ nanoslab (W110) are examined by the XPS as shown in Fig. (4). The wide range survey scans of WO$_3$ (Fig. S1) shows the presence of W and O. Moreover, the deconvoluted XPS spectra of doublet W (4f) comprises of W 4f$_{7/2}$ and W 4f$_{5/2}$ at a binding energy of 35.6 eV and 37.63 eV shows spin-orbit splitting of W (4f) level and corresponds to the W$^{+6}$ state (Fig. 4(a)). Nevertheless, the low-intensity peaks at 33.92 eV and 37.21 eV are demonstrating the presence of W$^{+5}$ state, which illustrates the existence of oxygen vacancy in WO$_3$ matrix. Furthermore, the deconvoluted spectra of O1s (Fig. 4(b)) show two peaks at 531.1 eV and 531.9 eV assigns to the presence of lattice oxygen (O$_2^-$) and adsorbed oxygen (O$^-$ and O$_2^-$). These multi-oxidation states of W and surface oxygen attributed to the enhanced electrochemical properties of WO$_3$ slabs.$^{55}$

The porosity and surface area of W70, W90 and W110 were examined by Brunauer–Emmett–Teller (BET) analysis (Fig. 5). The samples W110, W90 and W70 exhibit the same Langmuir (III) nitrogen adsorption-desorption isotherm with the surface area of 68.8 m$^2$g$^{-1}$, 49.3 m$^2$g$^{-1}$ and 34.8 m$^2$g$^{-1}$ respectively. The pore size distribution of the same sample was investigated by the Barrett-Joyner-Halenda (BJH) method as shown in the inset of Fig. 5. This illustrates the micro-porous nature with the pore size in the range of 1-3 nm. Thus, owing to the high surface area of sample W110 ensure the active sites for effective electrochemical process and effectively enhanced rate performance with storage capability.$^{56}$

3.2. Electrochemical performance of hydrated WO$_3$ nanoslabs

The electrochemical performance of electrode W70, W90 and W110 were carried out by the three-electrode system in 1M H$_2$SO$_4$ electrolytes between potential windows -0.6 to 0 V. The Fig. 6(a) exhibits the superimposed cyclic voltammetry (CV) curve of electrode W70, W90 and
W110 at low scan rate 2 mVs\(^{-1}\). It displays the higher current contribution of W110 with greater area under the curve signposts the better electrochemical charge storage performance than electrode W70 and W90. However, the electrode W110 and W90 are more faradic in nature than electrode W70, revealing the highly pseudocapacitive charge storage mechanism. The resulting anodic and cathodic waves at low scan rate 2 mVs\(^{-1}\) between the potential -0.45 V to -0.35 V and -0.35 V to -0.5 V of W90 and W110 exhibits the more active surface sites and reversible redox reaction \(\ce{W^{5+}/W^{6+}}\) accompanied with a dominated proton (H\(^+\)) insertion/de-insertion pseudocapacitive process.\(^{57-59}\) Fig. S2 shows the CV curves at various scan rates from 2-100 mVs\(^{-1}\) of electrodes W70, W90 and W110. It demonstrates at high scan rate 100 mVs\(^{-1}\) the cathodic and anodic redox waves are fade out due to the fast movement of proton under the high scan rate ensuing less interaction time at the electrode surface and/or low intercalation into WO\(_3\) crystalline layers.\(^{55}\) The compared specific capacitances of W70, W90 and W110 samples at various scan-rates are shown in Fig. 6(b). At a lower scan rate of 2 mVs\(^{-1}\), the specific capacitance of electrode W110 has reached to 386 Fg\(^{-1}\), which is higher than the specific capacitance of 315 Fg\(^{-1}\) and 254 Fg\(^{-1}\) of W90 and W70 respectively. This highest specific capacitance of the electrode W110 is compared with the various structures of WO\(_3\) as listed in Table 1. Similarly, the galvanostatics charge-discharge (GCD) curves were recorded at various current densities from 1 Ag\(^{-1}\) to 10 Ag\(^{-1}\) as shown in Fig. S3. These GCD curves demonstrating the deviation from the triangular line between potential ranges -0.3 V to -0.5 V, implying the capacity mainly arises by faradic redox reaction confirming CV findings. Fig. 6(c) shows the discharge profile at current density 2 Ag\(^{-1}\), which presents the highest discharge time of electrode W110 signifying the highest storage capacity than W70 and W90. In comparison, the electrode W110 show the highest specific capacitance of 367 Fg\(^{-1}\) than W90 (310 Fg\(^{-1}\)) and W70 (241 Fg\(^{-1}\))
at high current density 1 Ag\(^{-1}\) (Fig. 6(d), Fig. S3(d)). Interestingly, the capacitance values estimated from CV and GCD do not show any significant change in specific capacitance.

3.3. Charge storage kinematics

The current contribution in the CV curve is related to the respective scan rate according to equation (4).

\[
I = a \times v^b
\]  

(4)

Where, \(I\) is current, \(a\) is constant, \(v\) is scan rate and \(b\) is a constant value which can be 0.5 or 1.

The \(b\)-value is evaluated by the slop of linear fitting of log (current, \(I\)) vs log (scan rate, \(v\)). The dependency of current in the CV curve could be varied as either \(v^{0.5}\) or \(v\), which represents the semi-infinite diffusion process or dominated capacitive charge storage kinetics respectively.\(^{60}\)

The electrode W110 shows the lowest anodic \(b\)-value (Fig. 7(a)) of 0.84 than electrode W70 and W90 are 1.2, 1.1 respectively. Moreover, the electrode W110 clearly demonstrates the lowest \(b\)-value at various potential ranges between -0.1V to -0.6V (Fig. 7(b)) than electrode W70 and W90. It authorizes the significant proton insertion into the 2D structure of the slab (W110). Therefore, the highest specific capacitance of slab (W110) than nanosheets (W70 and W90) originated from the dominated proton insertion/deinsertion into the crystalline layer has realized.

Furthermore, the trasatti procedure has been utilized to discrete the current contributions by EDLC and proton insertion from the total capacitance using equation (5).\(^{61-62}\)

\[
Q(v) = Q_c + kv^{-1/2}
\]  

(5)

Where, \(Q_c\) is capacitance contribution from EDLC, \(k\) is constant, \(v\) is scan rate and \(Q(v)\) is charge store at scan rate \(v\). The Charge storage due to EDLC across the interface of electrode and electrolyte (\(Q_c\)) were evaluated by the intercept of the plot of \(Q(v)\) vs \(v^{-1/2}\) (Fig. S4), is almost 25
Cg\(^{-1}\), 55 Cg\(^{-1}\) and 74 Cg\(^{-1}\) of electrodes W70, W90 and W110 (Fig. 7(c)) respectively. The highest value of \(Q_c\) for electrode W110 correlated to have a high surface area than W70 and W90. Moreover, the proton insertion contribution of electrodes with respect to scan rate can be evaluated by subtracting the surface stored charges values from total stored charges at various scan rates that are bared in Fig. 7(d). This illustrates the capacity arises due to proton insertion into the crystalline layer is found to be 230 Cg\(^{-1}\) which is four times higher than EDLC contribution 75 Cg\(^{-1}\) at low scan rate 2 mVs\(^{-1}\). However, at high scan rate 50 mVs\(^{-1}\) the proton insertion capacity is accounted to be 54 Cg\(^{-1}\) which highlights the proton insertion pseudocapacitance is promising at a low scan rate than high scan rate.\(^{63-64}\)

Additionally, the cyclic stability test of electrode W70, W90 and W110 were carried out using the galvanostatic charge discharge (GCD) at high current density 5 Ag\(^{-1}\) as shown in Fig. 8(a). The electrode W110 shows comparatively high capacitance retention of 96% than W90 (89%) and W70 (86%) after 3000 cycles. It is noted that no significant variation in cyclic stability was observed in electrode W70, W90 and W110 due to the advantage of the morphology and role of the confined hydrate into the crystalline-layered structure enables the rapid movement of a proton. Furthermore, to better understand the charge transfer mechanism across the interface of electrode-electrolyte of all samples, the electrochemical impedance spectroscopy (EIS) was carried out (Fig. S5). The obtained electrochemical series resistance (\(R_{ESR}\)) at high frequency region is 3.2 \(\Omega\), 2.4 \(\Omega\), and 1.09 \(\Omega\) of W70, W90 and W110 respectively. Whereas, the electrode W70 and W90 exhibits the semi-circle (Fig. 8(b)) representing the charge transfer resistance (\(R_{ct}\)) across the interface of electrode-electrolyte, which is 54 \(\Omega\) and 36 \(\Omega\) respectively. The inset of Fig. 8(b) shows the equivalence circuit diagram with the impedance and resistance contributions to the electrochemical system.
Interestingly, the slab (electrode W110) inhibits the $R_{ct}$ with lower $R_{ESR}$ demonstrating the smaller internal resistance and resulting in the faster kinetics of redox reaction with highly conductive than electrode W70 and W90.

4. Conclusion

In summary, tuning the morphology and crystallinity from hydrated $\text{WO}_3$ nanosheets to high crystalline hydrated $\text{WO}_3$ slabs via increasing synthesis temperatures from 70 to 110 ºC is successfully achieved. The obtained 3D hydrated $\text{WO}_3$ slabs exhibit the enhanced specific capacitance of 386 Fg$^{-1}$ than 2D hydrated $\text{WO}_3$ nanosheets (254 Fg$^{-1}$) at scan rate 2 mVs$^{-1}$. This improved performance of hydrated $\text{WO}_3$ slabs is attributed to the enriched crystalline structure, enlarge the surface area, enhanced the active surface sides and effective proton insertion into a layered structure, which is resulting in the high redox pseudocapacitive mechanism. Therefore, the 3D highly crystalline $\text{WO}_3$ with confined hydrate into the layered structure is a potential candidate for high-rate intercalated pseudocapacitor.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Supporting Information is available from the journal or from the author.

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Fig. 1 (a) XRD spectra of W70, W90 and W110 and inset of the same figure shows the zoom area of plane (111), (b) Schematics crystal structure of hydrate WO$_3$H$_2$O, (c) Raman spectra of W70, W90 and W110, (d) TGA plots of W70, W90 and W110.
Fig. 2 (a, b) Low and high magnification FESEM images of nanosheets (W70), (c, d) Low and high magnification images of nanosheets (W90), (e, f) Low and high magnification images of slab (W110).
Fig. 3 (a, b) Low and high magnification TEM images of slab (W110), (c) IFFT images, (d) Intensity profile of selected region of figure (c), (e) SAED pattern of W110.
Fig. 4. XPS spectra of WO$_3$ nanoslabs (W110): Deconvoluted spectra of W 4f (a) and O 1s (b).
Fig. 5. Nitrogen adsorption-desorption isotherm and inset figure shows the pore size distribution of W70, W90 and W110; pore diameter unit is (a.u.) = Å (Angstrom).
Fig. 6 (a) Compared CV curve of W70, W90 and W110 at scan rate 2 mVs$^{-1}$, (b) Specific capacitance at various scan rates, (c) Galvanostatics discharge curves of W70, W90 and W110 at current density 2 Ag$^{-1}$, (d) Specific capacitance at various current densities.
Fig. 7 Charge storage kinematics: (a) anodic peak potential b- values, (b) b- values calculated at various potentials, (c) EDLC contribution by W70, W90 and W110, (d) EDLC and H\(^+\) ions insertion contributions of electrode W110 at various scan rates.
Fig. 8 (a) Cyclic stability, (b) Impedance plot at high frequency region and inset is equivalence circuit diagram of W70, W90 and W110.
Table 1: Performance comparison of various nanostructure and crystal structure of WO₃.

| Material          | Method                  | Morphology | Crystal structure | Specific capacitance | Stability           | Ref. |
|-------------------|-------------------------|------------|-------------------|----------------------|---------------------|------|
| WO₃               | Hydrothermal            | Cube       | Hexagonal         | 377.5 F g⁻¹          | 90% after 4000 cycle | 35   |
| WO₃ NRs/rGO       | Hydrothermal            | Nanorod    | Hexagonal         | 343 F g⁻¹           | 92% after 1000 cycle | 54   |
| WO₃               | Hydrothermal            | Nanoplate  | Monoclinic        | 334 F g⁻¹           | 91% after 5000 cycle | 61   |
| WO₃               | Hydrothermal            | Nanorod    | Hexagonal         | 385 F g⁻¹           | 89% after 1000 cycle | 65   |
| WO₃⁻WO₃·0.5H₂O    | Microwave-assisted hydrothermal | Disordered nanorods | Hexagonal + cubic | 293 F g⁻¹ | NA                  | 66   |
| Bi₂WO₆            | Sonochemical            | Nanoparticle | Amorphous        | 304 F g⁻¹          | 200 cycle          | 67   |
| m-WO₃             | Template-assisted synthesis | Mesoporous   | Cubic             | 199 F g⁻¹          | 1000 cycle         | 68   |
| m-WO₃⁻x Cₓ        | Block-polymer-assisted synthesis | Hexagonal porous | Triclinic       | 103 F g⁻¹          | NA                  | 69   |
| WO₃/rGO           | Hydrothermal            | Nanosheets  | Hexagonal         | 244 F g⁻¹          | 97% after 900 cycle | 70   |
| WO₃               | Hydrothermal            | Nanoparticle | NA                | 113                 | 68.5% after 2000 cycle | 71  |
| WO₃               | Hydrothermal            | Nanorod    | Hexagonal         | 155.5               | 84.9% after 5000 cycle | 72   |
| 3D WO₃ slab       | Wet chemical           | Nanoslab   | Orthorhombic      | 386 F g⁻¹          | 96% after 3000 cycle | This work |

This work
The morphology tuning with respect to synthesis temperature shows 2D nanosheets conversion into 3D slabs with improved crystallinity. The enhanced supercapacitor performance of 3D slab attributed to the promising proton insertion into layered crystal structure.