



Cite this: *Nanoscale Adv.*, 2025, 7, 4450

## WO<sub>3</sub>/Nb<sub>2</sub>CT<sub>x</sub> MXene 2D–2D heterojunction as a high performance photoanode for photoelectrochemical water splitting†

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Photoelectrochemical (PEC) water splitting plays a key role in the production of green hydrogen, which is a sustainable energy source and non-exploitative to the environment. Therefore, the development of efficient photocatalysts is essential for enabling green hydrogen generation. In this work, the synergistic effect between tungsten oxide (WO<sub>3</sub>) and Nb<sub>2</sub>CT<sub>x</sub> (MXene) was explored for PEC water oxidation, and a composite catalyst was prepared using a hydrothermal and sonication approach to obtain a 2D/2D WO<sub>3</sub>/Nb<sub>2</sub>CT<sub>x</sub> heterojunction. WO<sub>3</sub> is a promising photocatalyst owing to its optimal band gap, stability, and cost-effectiveness, but its efficiency is hindered by poor charge transfer, rapid recombination, and weak visible light absorption. Integrating Nb<sub>2</sub>CT<sub>x</sub>, a highly conductive MXene, enhances charge separation, reduces electron–hole recombination, and strengthens photocatalytic activity. This synergy increases the number of catalytic sites, improves visible light absorption, and stabilizes WO<sub>3</sub>, leading to a more efficient and durable material for solar energy conversion and water splitting. The Tauc plot of the composite shows a slightly lower bandgap (2.56 eV) than that of pristine WO<sub>3</sub> (2.74 eV), while the charge separation efficiency of the composite is confirmed by its lower photoluminescence intensity than that of pristine WO<sub>3</sub>. Among the synthesized catalysts, WO<sub>3</sub>@Nb<sub>2</sub>C3 showed improved PEC-OER activity by attaining a photocurrent density of 4.71 mA cm<sup>-2</sup> at 1.23 V vs. RHE compared to the pristine WO<sub>3</sub> that attained a photocurrent density of 2.15 mA cm<sup>-2</sup> at the same potential. This strategy appears promising for designing catalysts for PEC water oxidation in a solar-driven hydrogen-powered future.

Received 12th April 2025

Accepted 21st May 2025

DOI: 10.1039/d5na00345h

rsc.li/nanoscale-advances

## 1. Introduction

The environment has been severely degraded because of the widespread reliance on non-renewable energy sources, such as coal, oil, and natural gas. Burning fossil fuels as a continuous energy source has become hazardous to the environment, as it is the main cause of global warming, air contamination, extreme weather patterns, and ecosystem deterioration, making life less sustainable on the planet. Therefore, there is an urgent global need to transition to cleaner and renewable energy sources such as wind, hydropower, and solar energy.<sup>1,2</sup> Photoelectrochemical (PEC) water splitting is the process of generating green hydrogen *via* the electrolysis of water using solar energy. PEC water splitting is a great substitute for nonrenewable energy sources because it produces green hydrogen without dependence on fossil fuels; hence, it is a great technique for producing clean energy, as it assures a more

environmentally friendly, sustainable, and resilient hydrogen-powered future.<sup>3,4</sup> Therefore, stable, abundant, and cost-effective photocatalysts are required to conduct photoelectrochemical water splitting efficiently. Some important parameters to consider when choosing an efficient photocatalyst include light harvesting efficiency, band gap energy, easy transfer of electrons from the valence band to the conduction band and less electron–hole recombination.<sup>2</sup> Various studies have been conducted on different photocatalysts such as BiVO<sub>4</sub>,<sup>5</sup> CdS,<sup>6</sup> Bi<sub>2</sub>WO<sub>6</sub>,<sup>7</sup> WO<sub>3</sub>,<sup>8</sup> and g-C<sub>3</sub>N<sub>4</sub>.<sup>9</sup> These efficient catalysts, however, suffer from limited visible light absorption, faster charge recombination and poor stability. To overcome these problems, the formation of heterostructures has been reported, for example, with BiVO<sub>4</sub>,<sup>10,11</sup> TiO<sub>2</sub>,<sup>12–15</sup> Fe<sub>2</sub>O<sub>3</sub>,<sup>16,17</sup> ZnO,<sup>18</sup> silicon-based n–i–p heterojunction<sup>19</sup> and surface engineering for defect passivation/reduction.<sup>20</sup> WO<sub>3</sub> has attracted significant interest among them because it has many aspects that make it an ideal candidate for use as a photoanode material. Bulk WO<sub>3</sub> is an n-type semiconductor material with an indirect band gap of 2.4–2.8 eV, where the filled O 2p orbital forms the valence band, while the conduction band is formed by the empty W 5d orbital.<sup>21,22</sup> With visible light absorption coverage of 12% of the energy range of the solar spectrum, it offers chemical stability, straightforward synthesis,

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d5na00345h>



strong photocatalytic oxidizing ability, cost effectiveness, abundance, and non-toxicity.<sup>23</sup> However,  $\text{WO}_3$  is susceptible to photo corrosion, and bare tungsten oxide has quite a low photocatalytic activity because of faster electron–hole recombination; there is a need to develop a strategy for overcoming these problems and enhancing the photocatalytic activity of  $\text{WO}_3$ .<sup>22</sup> In the literature, many strategies have been employed to enhance the photocatalytic performance of  $\text{WO}_3$ , such as morphological engineering, modification through doping with various elements, oxygen vacancy studies,<sup>23,24</sup> and crystal phase control.<sup>25</sup> One of the strategies is to form composites with suitable semiconductor materials to create heterostructures that can result in an increased number of active sites, increased surface area and enhanced photocatalytic efficiency of tungsten oxide by an increase in the rate of charge separation and decrease in the rate of electron–hole recombination.<sup>26–28</sup> A class of 2D materials called MXenes are transition metal carbides or nitrides with the general formula  $\text{M}_{n+1}\text{X}_n\text{T}_x$ , where  $n$  is a number from 1 to 3, M is a transition metal, X is the carbide or nitride, and  $\text{T}_x$  is the surface functional group, which is usually  $-\text{F}$ ,  $-\text{OH}$ , or  $-\text{O}$ . MXenes are obtained from the MAX phase by the process of etching through the removal of the “A” layer (Al, Ge, or Si).<sup>29</sup> MXene can prove to be a great choice for creating heterostructures with  $\text{WO}_3$  because of its high conductivity, structural support and stability, photostability, hydrophilicity, and corrosion-resistant nature.<sup>30,31</sup> MXenes have multiple exposed metal sites, many surface groups and layered structures; all these properties agree with the formation of a heterostructure of MXene and  $\text{WO}_3$  to improve the overall photocatalytic activity of  $\text{WO}_3$  for PEC water oxidation. A few studies have reported composite formation using MXene with  $\text{WO}_3$ ; for example,  $\text{ZnO}/\text{WO}_3/\text{Ti}_3\text{C}_2$  has been tested for PEC water splitting.<sup>32</sup> Another study reported the use of  $\text{Ti}_3\text{C}_2$  MXene/ $\text{WO}_3$  for photodegradation studies of tetracycline antibiotics, and the composite was synthesized using *in situ* growth of  $\text{WO}_3$  nanosheets on the MXene surface in a one-pot solvothermal synthesis strategy.<sup>33</sup> In another similar study, hydrothermal and ultrasonic treatments were used to develop a 2D/2D  $\text{WO}_3/\text{Ti}_3\text{C}_2$  heterojunction and were used for the photocatalytic degradation of methylene blue dye under visible light irradiation.<sup>34</sup> Similarly, a  $\text{WO}_3/\text{MXene}$  ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) composite was reported earlier using electrostatic attraction between  $\text{WO}_3$  nanorods and MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) for supercapacitor applications.<sup>35</sup> Few studies have been conducted on different kinds of MXene, such as niobium carbide, vanadium carbide, or molybdenum carbide, and there is still room for investigating them as PEC catalysts. In previous studies, niobium carbide MXene has been used as a photoactive material and for charge storage in the literature.<sup>36</sup> In this study,  $\text{WO}_3$  nanorods and niobium carbide ( $\text{Nb}_2\text{CT}_x$ ) MXene composites are prepared by applying the hydrothermal method, followed by sonication. The synergistic effect of  $\text{WO}_3$  and  $\text{Nb}_2\text{CT}_x$  is explored, where both the components of the heterostructure complement the photocatalytic properties and surface characteristics of each other, resulting in enhanced photoelectrochemical OER activity.  $\text{Nb}_2\text{CT}_x$  facilitates charge extraction, while  $\text{WO}_3$  provides an electronic structure that drives the water oxidation reaction

efficiently.  $\text{WO}_3$ , which is susceptible to photo corrosion, can undergo photo corrosion during the water oxidation reaction, but it is protected by  $\text{Nb}_2\text{CT}_x$  because it stabilizes the surface of  $\text{WO}_3$  and has a noncorrosive nature and tungsten oxide is not degraded over time and therefore has enhanced stability. Hence, the interaction of tungsten oxide with niobium carbide seems promising, as it can result in increased light absorption efficiency, enhanced charge separation, decreased electron–hole recombination, increased number of catalytic sites, prolonged stability, and enhanced interface contact surface area. This study is expected to serve as a pathway for designing highly efficient photocatalysts driven by visible light. The as-prepared samples were characterized using powder XRD, XPS, FESEM/EDX, HRTEM, and PL techniques.

## 2. Experimental

### 2.1. Materials and chemicals

Ammonium metatungstate, hydrochloric acid (HCl), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), and hydrofluoric acid (HF) were purchased from Sigma-Aldrich. The MAX phase ( $\text{Nb}_2\text{AlC}$ ) was purchased from Chemazone, Inc. Nanochemazone. Fluorine-doped tin oxide (FTO) plates were obtained from Sigma-Aldrich. Deionized water was used to prepare the electrolytes and reaction mixtures.

### 2.2. Synthesis of $\text{WO}_3$

$\text{WO}_3$  nanorods were synthesized by applying the hydrothermal method, in which 0.77 g of ammonium meta tungstate was dissolved in 12.5 ml distilled water and 0.53 ml hydrochloric acid was added to it. The homogenized mixture was then transferred into a Teflon-lined autoclave and kept at 180 °C for 4 hours. After centrifugation and washing at 5000 rpm with distilled water three times, the material was kept at 70 °C for 6 hours and then kept for annealing at 500 °C for half an hour, and yellowish powder was formed.<sup>37</sup>

### 2.3. Synthesis of $\text{Nb}_2\text{CT}_x$

Two grams of  $\text{Nb}_2\text{AlC}$  were slowly added into 40 ml of HF, and the solution was magnetically stirred at room temperature for 90 hours.<sup>38</sup> After this period, the material was washed through centrifugation at 5000 rpm multiple times with DI water. The washed material was then kept for drying overnight at 60 °C.

### 2.4. Synthesis of $\text{WO}_3/\text{Nb}_2\text{CT}_x$ heterojunction

$\text{WO}_3/\text{Nb}_2\text{CT}_x$  heterojunction was prepared by applying the sonication approach. 100 mg of hydrothermally prepared  $\text{WO}_3$  was dissolved in 10 ml of DI water, and  $\text{Nb}_2\text{CT}_x$  sheets were added to it (5, 10, and 15 weight%). The solution was kept at sonication for 12 hours; then, the resulting suspension was dried overnight at 100 °C.<sup>34</sup> The resulting materials were named  $\text{WO}_3@\text{Nb}_2\text{C}1$ ,  $\text{WO}_3@\text{Nb}_2\text{C}2$ , and  $\text{WO}_3@\text{Nb}_2\text{C}3$  for 5, 10, and 15 weight% of  $\text{Nb}_2\text{CT}_x$ , respectively. The ultrasonication approach is beneficial for synthesizing such heterojunctions because high shear forces generated by intense sound waves can be helpful in the uniform distribution of particles and can break the



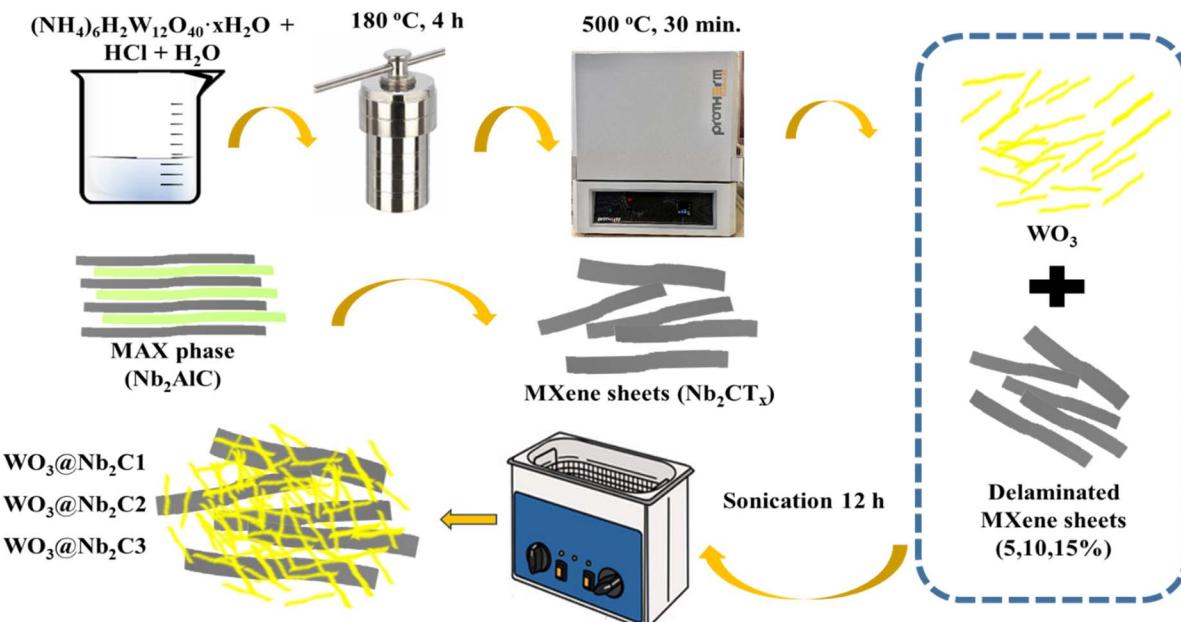


Fig. 1 Schematic of the synthesis showing pure  $\text{WO}_3$ ,  $\text{Nb}_2\text{CT}_x$  MXene and composite  $\text{WO}_3@\text{Nb}_2\text{CT}_x$  formation.

agglomerates of particles to ensure uniform dispersibility. As a result of ultrasonic treatment, bubbles are formed, and these bubbles rupture swiftly and hence induce local high temperature and pressure within the material, which ultimately can induce surface modification in both  $\text{WO}_3$  and  $\text{Nb}_2\text{CT}_x$ . A schematic of the synthesis is depicted in Fig. 1.

## 2.5 Photoelectrochemical characterization and preparation of the working electrode

Catalyst ink was prepared by applying the spin coating method, and FTO was used. For cleaning, the FTO was immersed in acetone, ethanol, and DI water for 15 minutes in each solvent. 100 mg of the prepared photocatalyst was added into 5 ml of ethanol ( $20 \text{ mg ml}^{-1}$ ) to prepare a slurry. This dispersion (1000 microliters) was spin coated at 1000 rpm on FTO substrates to procure  $\text{WO}_3$  and  $\text{WO}_3@\text{Nb}_2\text{C}$  thin films, which were dried at  $60^\circ\text{C}$  for 5 min. A thin uniform film was then obtained by repeating the coating and drying for 5 cycles. All PEC measurements were performed using an electrochemical workstation (Biologic VSP-300 Potentiostat) with three-electrode cell configurations: platinum wire as the counter electrode,  $\text{Ag}/\text{AgCl}$  as the reference electrode, and catalyst-coated FTO as the working electrode. The experiment was performed in a quartz cell. As the light source solar simulator, Oriel LCS-100 with a 100 W Xe lamp and 1.0 sun AM 1.5 G filter was used. The electrolyte used was a 0.5 M  $\text{Na}_2\text{SO}_4$  solution. The Nernst equation was used for the conversion of potential to *vs.* RHE. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) measurements were performed in the potential range of 0.6–1.6 V *vs.* RHE under illumination and in the dark as well. Chopped light LSVs were also performed in the potential range of 0.6–1.6 V *vs.* RHE at a scan rate of 5 mV s<sup>-1</sup> using a mechanical chopper with 5 seconds light ON and 5 seconds

light OFF intervals. Electrochemical impedance spectroscopy (EIS) was performed under illumination in the frequency range of 100–100 mHz at a potential of 0.8 V *vs.* RHE. Electrochemical surface area (ECSA) and double layer capacitance ( $C_{dl}$ ) were calculated by taking CV cycles in the dark in the non-faradaic potential range at various scan rates. The Mott–Schottky analysis was performed to determine the flat band potential and donor density.

## 3 Results and discussion

### 3.1 Characterizations

The synthesis of all the materials was studied by powder X-ray diffraction (XRD), and the XRD was recorded in the range of  $2\theta$  5–70°. The etching of the commercially available niobium aluminum carbide ( $\text{Nb}_2\text{AlC}$ ) MAX phase to  $\text{Nb}_2\text{CT}_x$  MXene was confirmed by XRD patterns, as illustrated in Fig. S1.† The MAX phase shows a prominent diffraction pattern at the  $2\theta$  values of 12.7° (002), 33.3° (100), 38.7° (103), 39.1° (006), and 52.3° (106) of crystalline  $\text{Nb}_2\text{AlC}$ , which matches well with the standard pattern (JCPDS 30-0033) (Fig. S1†).<sup>38,39</sup> After treatment with HF to etching the Al layer, a characteristic broad signal was observed at a  $2\theta$  value of 8.9°, which corresponds to the (002) crystal plane of  $\text{Nb}_2\text{CT}_x$  MXene, corresponding to the *d*-spacing of 0.98 nm, similar to the previously reported study.<sup>40</sup> The appearance of this new signal as well as the substantial decrease in the intensity of the diffraction signal at 39° (006); others confirm the formation of  $\text{Nb}_2\text{CT}_x$  MXene after successful etching.<sup>38,40</sup> The synthesis of  $\text{WO}_3$  is confirmed by analyzing the XRD pattern, showing the prominent signals at  $2\theta$  values of 23.1°, 23.5°, 24.4°, 33.3°, 33.6°, 34.2°, and 49.9° and it matches well with the standard pdf # 431035 (Fig. 2a) and shows the monoclinic phase of the  $\text{WO}_3$ .<sup>22</sup> The synthesis of  $\text{WO}_3@\text{Nb}_2\text{CT}_x$



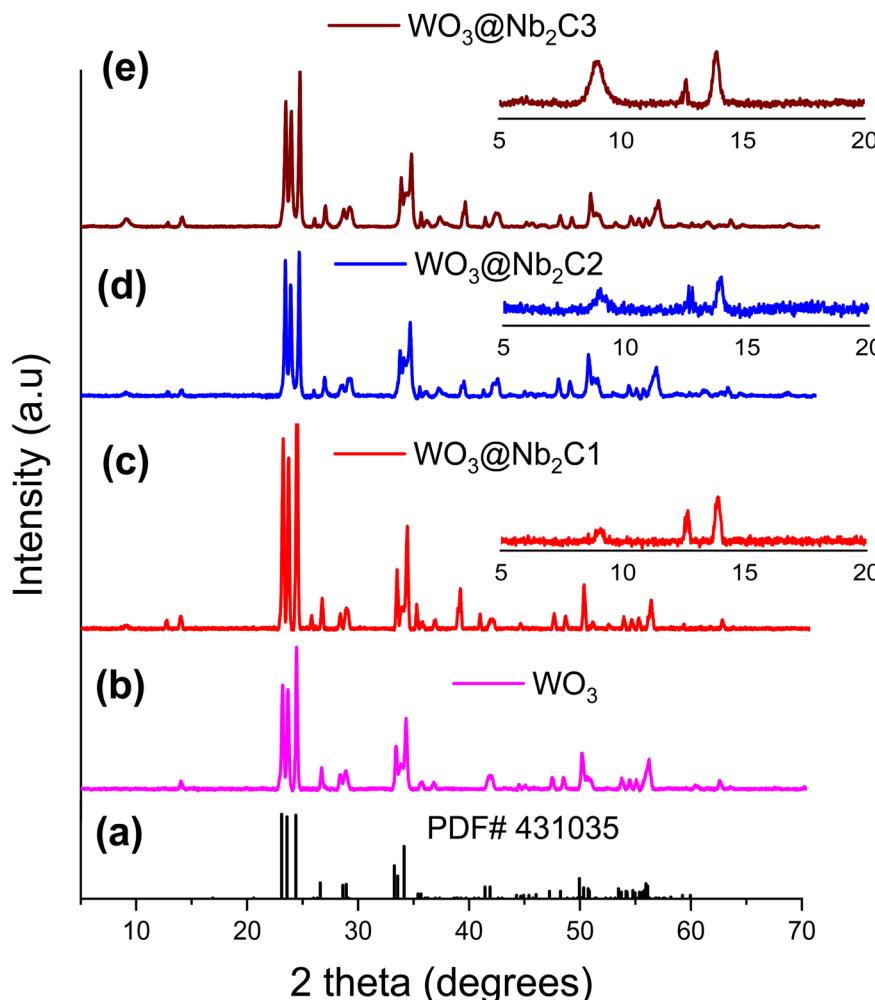


Fig. 2 XRD patterns of the WO<sub>3</sub> reference card (a), WO<sub>3</sub> (b), WO<sub>3</sub>@Nb<sub>2</sub>C1 (c), WO<sub>3</sub>@Nb<sub>2</sub>C2 (d), and WO<sub>3</sub>@Nb<sub>2</sub>C3 (e). The insets show the magnified patterns of (c)–(e).

heterojunction with different ratios of Nb<sub>2</sub>CT<sub>x</sub> (5–15%) was also confirmed by the XRD pattern shown in Fig. 2(c–e), and the broad signal at 8.9 shows that the Nb<sub>2</sub>CT<sub>x</sub> is incorporated successfully to produce WO<sub>3</sub>@Nb<sub>2</sub>CT<sub>x</sub> composite with varying ratios.<sup>41</sup> The XRD of the composites shows no significant shift in WO<sub>3</sub> peaks, suggesting physical interfacial interaction between WO<sub>3</sub> and Nb<sub>2</sub>CT<sub>x</sub> MXene, similar to previously reported studies where composite synthesis was carried out through electrostatic attraction between WO<sub>3</sub> nanorods and Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene for supercapacitor applications.<sup>35</sup>

The syntheses of WO<sub>3</sub> and WO<sub>3</sub>@Nb<sub>2</sub>C3 composites were also confirmed by analyzing the XPS survey scan. Fig. 3 shows that all the desired elements (W, O, Nb, and C) are present on their respective binding energies, which shows the successful incorporation of Nb<sub>2</sub>CT<sub>x</sub> MXene with WO<sub>3</sub>. The absence of Al 2p and 2s signals at  $\approx$ 74 and  $\approx$ 118 eV in both survey scans also confirms successful etching.<sup>42</sup> The high-resolution spectra of W 4f core levels show a well-defined doublet at binding energies at 35.6 and 37.7 eV and can be assigned to W 4f<sub>7/2</sub> and W 4f<sub>5/2</sub> for W<sup>6+</sup> (Fig. 3b) and a weak doublet at 34.3 eV and 36.4 eV for W<sup>5+</sup>.<sup>33,43</sup> The high resolution XPS core level Nb 3d region shows

spin orbital splitting at binding energies of 203.3 and 206.1 eV, which corresponds to 3d<sub>5/2</sub> and 3d<sub>3/2</sub> of Nb–C bonds, respectively, for both Nb<sub>2</sub>CT<sub>x</sub> and WO<sub>3</sub>@Nb<sub>2</sub>C3 composite (Fig. 3c). Another week's broad doublet at 204.9 eV and 207.4 eV shows the presence of Nb–O bonds, as reported previously for Nb<sub>2</sub>CT<sub>x</sub> MXene.<sup>44,45</sup> The core level XPS of the O 1s region of WO<sub>3</sub> (Fig. 3d) shows the major peak fitting at 530.5 eV and 531.4, which can be assigned to lattice oxygen and oxygen absorbed on the surface, respectively.<sup>33</sup> In the case of WO<sub>3</sub>@Nb<sub>2</sub>C3 composite, O 1s spectra show other peaks at 531.6 and 533 eV, which can be assigned to C–Nb–O<sub>x</sub> and interlayer adsorbed water due to the presence of Nb<sub>2</sub>CT<sub>x</sub> MXene.<sup>30,45</sup>

Fig. S2† shows the FESEM images of the etched Nb<sub>2</sub>CT<sub>x</sub> MXene. It can be observed that the layered morphology of the Nb<sub>2</sub>CT<sub>x</sub> is present, and gaps in aluminum after etching are visible, which is a typical shape of 2D MXenes, as reported previously.<sup>30,46</sup> Fig. S3† shows the small plate-like structures of pristine WO<sub>3</sub> in the nanometer range (a) and flower-like arrangements when aggregated (b). During the composite formation, WO<sub>3</sub> was smoothly distributed over the surface of the delaminated layers of Nb<sub>2</sub>CT<sub>x</sub> to produce the WO<sub>3</sub>@Nb<sub>2</sub>C3



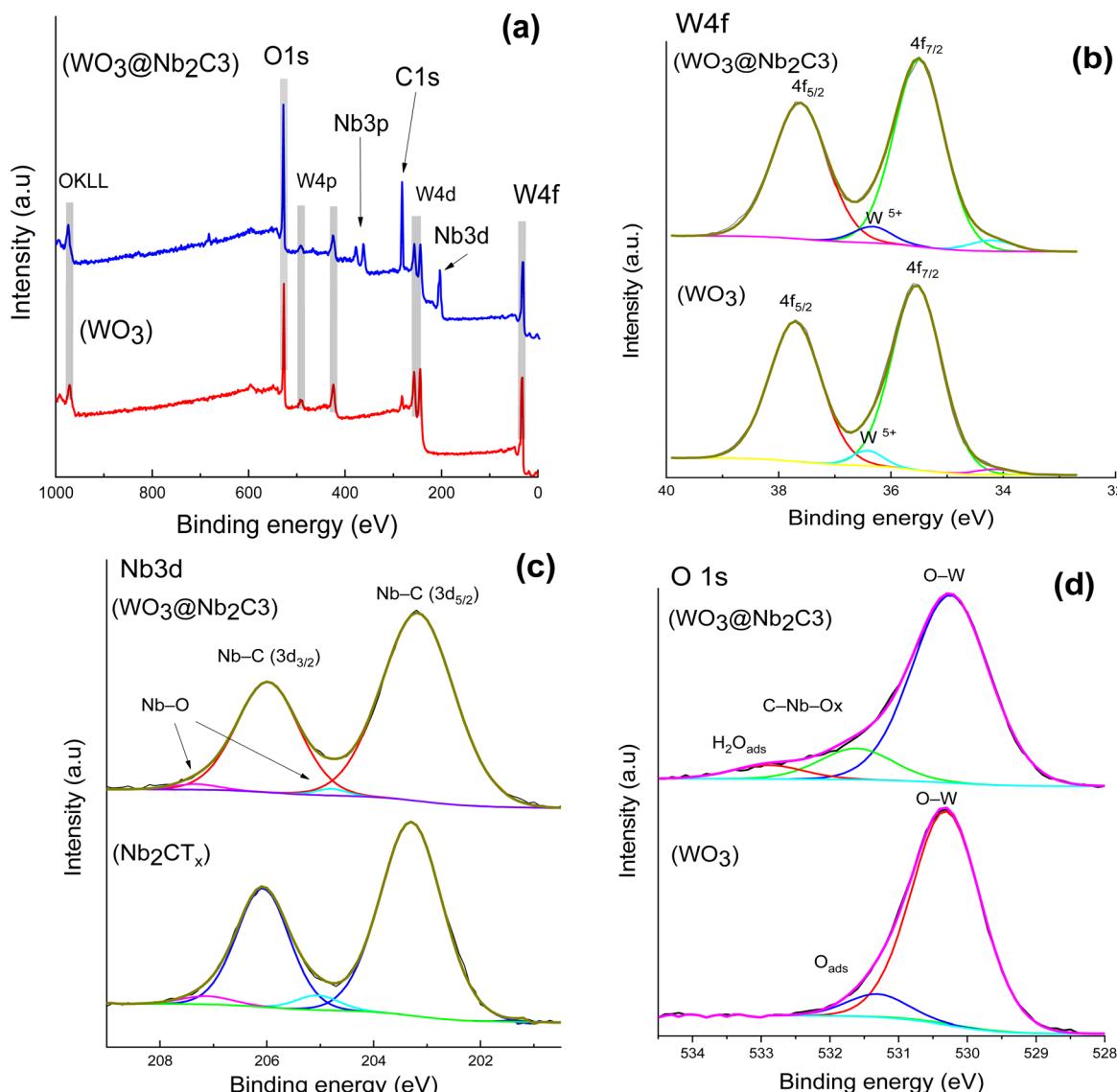


Fig. 3 XPS survey scan of  $\text{WO}_3$  and  $\text{WO}_3@\text{Nb}_2\text{C}3$  (a); high resolution XPS spectra of W 4f of  $\text{WO}_3$  and  $\text{WO}_3@\text{Nb}_2\text{C}3$  (b); high resolution XPS spectra of Nb 3d of  $\text{Nb}_2\text{CT}_x$  and  $\text{WO}_3@\text{Nb}_2\text{C}3$  (c); and high resolution XPS spectra of O 1s of  $\text{WO}_3$  and  $\text{WO}_3@\text{Nb}_2\text{C}3$  (d).

composite. The sharp edges of the nanoplate become smooth in the composite owing to sonication, as shown in Fig. 4(a) and (b). Fig. 4c shows the EDX spectrum of the  $\text{WO}_3@\text{Nb}_2\text{C}3$  composite with all the required component elements.

Fig. 5 shows TEM images of the composite. Both components of the composite  $\text{WO}_3$  and  $\text{Nb}_2\text{CT}_x$  MXene are visible (Fig. 5a), showing successful composite formation; the fringes on  $\text{Nb}_2\text{CT}_x$  MXene are clearly visible and are related to interlayer spacing.<sup>40</sup> The HRTEM (Fig. 5a) of  $\text{WO}_3@\text{Nb}_2\text{C}3$  composite shows the fringes corresponding to plane (002) of  $\text{Nb}_2\text{CT}_x$  MXene with a *d*-spacing of 0.98 nm, while the  $\text{WO}_3$  shows the fringes corresponding to plane (200) of monoclinic phase with *d*-spacing of 0.36 nm at the composite interface.<sup>47</sup>

The investigation of the optical absorption properties of  $\text{WO}_3$  and  $\text{WO}_3@\text{Nb}_2\text{C}3$  composite was carried out by UV-vis spectroscopy. The Tauc equation is used for the relation between the

bandgap energy and absorption spectra, which is written as follows:  $(\alpha h\nu) = k(h\nu - E_g)^n$ .

Extrapolating the linear portion of the plot ( $h\nu$ ) vs. energy ( $\alpha h\nu$ )<sup>2</sup> provides the band gap ( $E_g$ ) within a wavelength range of 200–800 nm. Various parameters can be employed to induce alteration in  $E_g$  values, including doping, grain size, annealing treatment, and the nature of transition (direct or indirect).<sup>48</sup> The bandgap energies of  $\text{WO}_3$  and  $\text{WO}_3@\text{Nb}_2\text{C}3$  composite were observed as 2.74 and 2.56 eV, respectively (Fig. 6a), which agrees with previously reported studies.<sup>33,47</sup> By the addition of  $\text{Nb}_2\text{CT}_x$  sheets to the catalyst, the band gap energy for  $\text{WO}_3@\text{Nb}_2\text{C}3$  is lower than that of  $\text{WO}_3$ , and it can be attributed to the overlapping of electronic band structures.<sup>47</sup> As the band gap energy is reduced, it is beneficial for the generation of electrons and holes in visible light, and  $\text{Nb}_2\text{CT}_x$  serves to prevent the recombination of electrons and holes, which ultimately results in the

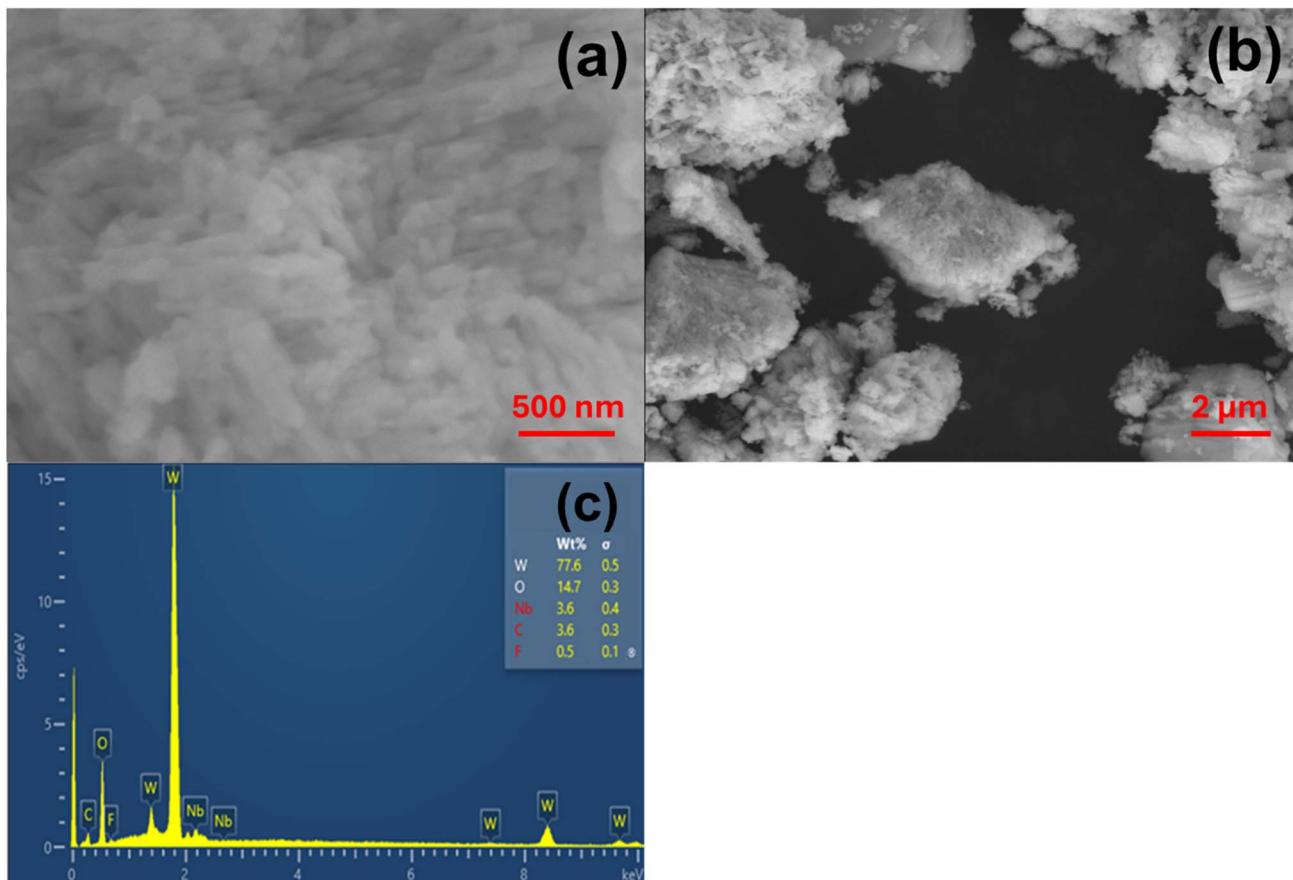


Fig. 4 FESEM images of the  $\text{WO}_3@\text{Nb}_2\text{C}_3$  composite at different resolutions (a and b) and EDX spectrum of the composite (c).

enhancement of the photoelectrocatalytic efficiency of  $\text{WO}_3@\text{Nb}_2\text{C}_3$ . Steady-state photoluminescence (PL) studies were conducted to interpret the behavior of photo-induced charge separation and recombination. Fig. 6b shows a broad emission peak under an excitation wavelength of 375 nm for

pristine  $\text{WO}_3$  at a signal centered at about 465 nm, which agrees with faster electron–hole pair recombination as a result of the de-excitation emission from W 4f to O 2p. Two other peaks of low intensity at 500 nm as a shoulder and 545 nm could arise owing to the band transition of the trapped electrons on defect

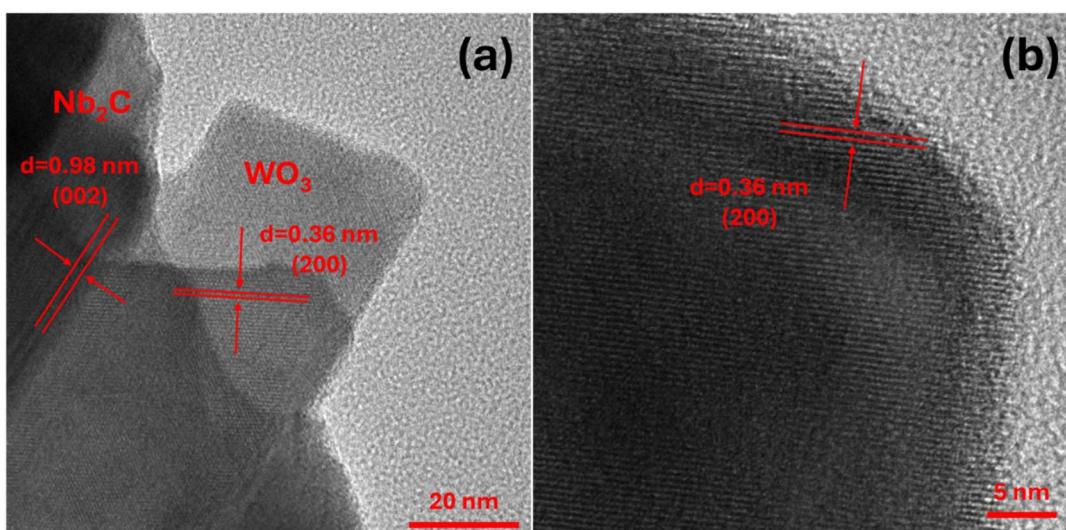


Fig. 5 TEM image of composite (a) at 20 nm and HRTEM image (b) at 5 nm.

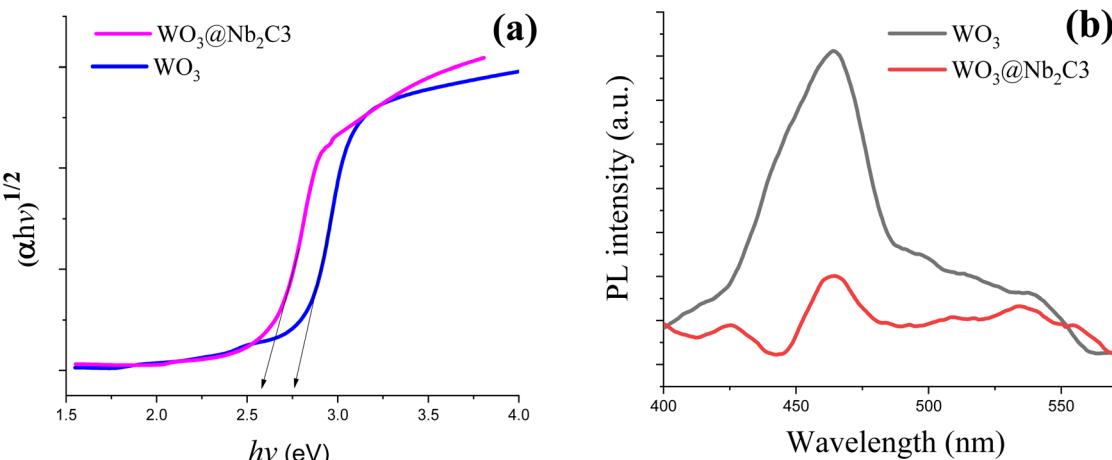


Fig. 6 Spectroscopic characterization of  $\text{Nb}_2\text{CT}_x$  MXene,  $\text{WO}_3$  and  $\text{WO}_3@\text{Nb}_2\text{C}3$  composites: (a) Tauc plots and (b) photoluminescence.

sites to the valence band, showing the role of  $\text{W}^{5+}$  species in  $\text{WO}_3$ , which is evident in the XPS results.<sup>33</sup> It is evident that the PL intensity significantly decreased upon the composite formation of  $\text{WO}_3@\text{Nb}_2\text{C}3$  compared to pure  $\text{WO}_3$ . This disparity in photoluminescence can be attributed to the boosted charge separation within the composite.<sup>23</sup> The quenching of photoluminescence intensity reveals that the assimilation of  $\text{Nb}_2\text{CT}_x$  MXene on  $\text{WO}_3$  possibly accelerates spatial charge separation and overturns carrier recombination through the establishment of a supplementary nonradiative decay pathway across the  $\text{WO}_3/\text{Nb}_2\text{CT}_x$  MXene interface.<sup>33</sup> The increased charge separation and reduced recombination rate make the material highly suitable for various photocatalytic applications.<sup>21</sup>

### 3.2 Photoelectrochemical studies

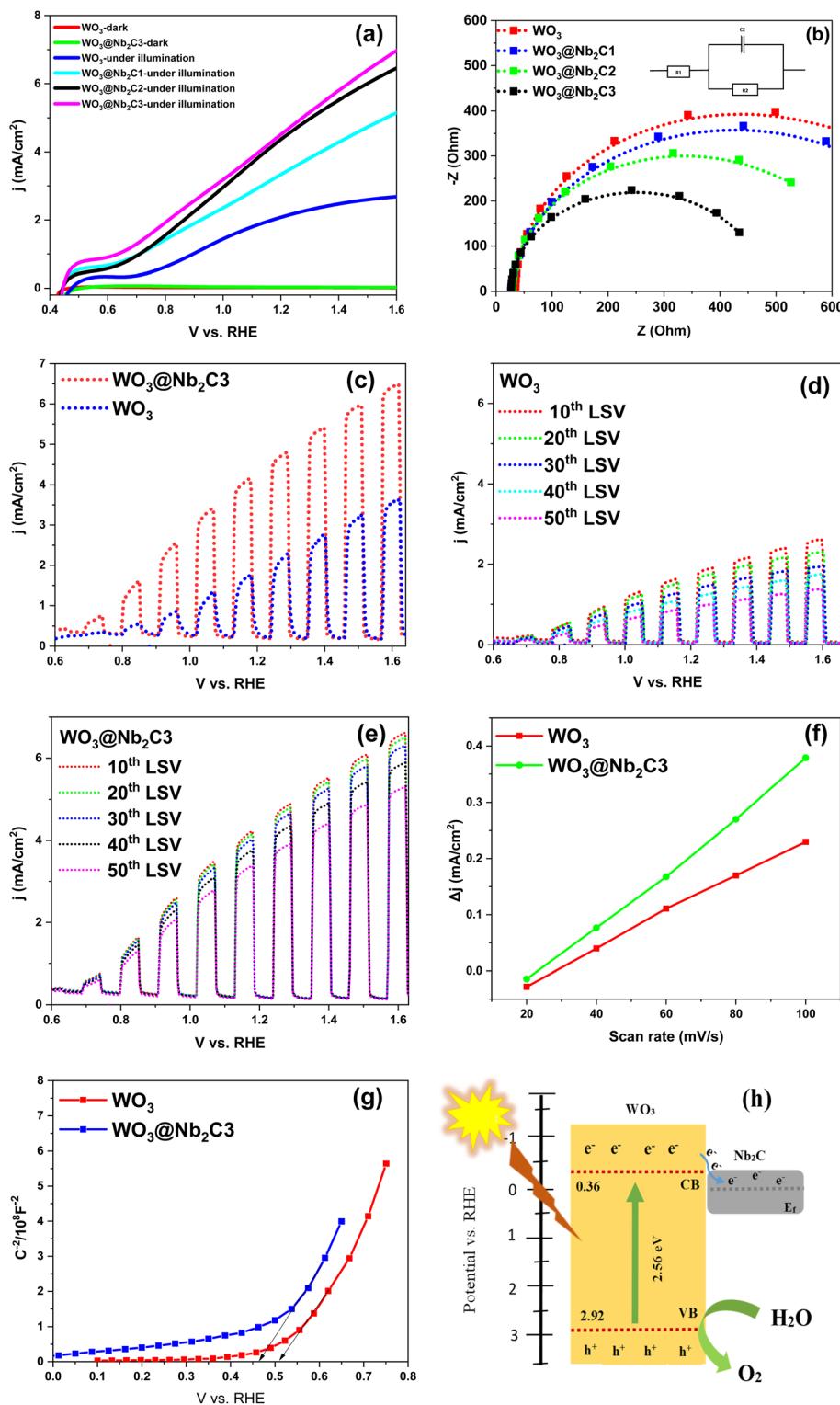
Photoelectrochemical catalytic activity was examined using an electrochemical workstation (Biologic VSP-300 potentiostat) with a 1.0 sun AM 1.5 G solar simulator as the light source in a 0.5 M  $\text{Na}_2\text{SO}_4$  electrolyte. This work preferred a hole scavenger-free electrolyte, as the presence of a sacrificial agent can interrupt and mask some important information about the photoelectrochemical experiment representations. LSV measurements were performed for  $\text{WO}_3$ ,  $\text{WO}_3@\text{Nb}_2\text{C}1$ ,  $\text{WO}_3@\text{Nb}_2\text{C}2$ , and  $\text{WO}_3@\text{Nb}_2\text{C}3$  under illumination and in the dark as well. Fig. 7a shows that  $\text{WO}_3$  photocatalytic activity is enhanced by forming a heterojunction with  $\text{Nb}_2\text{CT}_x$ . Among the three composites with varying ratios of  $\text{Nb}_2\text{CT}_x$ ,  $\text{WO}_3@\text{Nb}_2\text{C}3$  outperformed the other catalysts by attaining a photocurrent density of  $4.71 \text{ mA cm}^{-2}$  vs. 1.23 V RHE, while  $\text{WO}_3$ ,  $\text{WO}_3@\text{Nb}_2\text{C}1$ , and  $\text{WO}_3@\text{Nb}_2\text{C}2$  attained photocurrent densities of  $2.15 \text{ mA cm}^{-2}$ ,  $3.48 \text{ mA cm}^{-2}$ , and  $4.56 \text{ mA cm}^{-2}$  at 1.23 V RHE, respectively. The higher photocurrents demonstrate that more charge carriers pass through the circuit for reaction with water to evolve oxygen.

EIS was performed under illumination in frequencies ranging from 100 kHz to 100 mHz at a potential of 0.8 V vs. RHE, investigating the charge transfer resistance. Fig. 7b shows the

Nyquist plots for  $\text{WO}_3$ ,  $\text{WO}_3@\text{Nb}_2\text{C}1$ ,  $\text{WO}_3@\text{Nb}_2\text{C}2$ , and  $\text{WO}_3@\text{Nb}_2\text{C}3$ .  $\text{WO}_3@\text{Nb}_2\text{C}3$  has the smallest semicircle among them; the diameter of the semicircle is directly proportional to the  $R_{ct}$  value. The smaller the semicircle, the smaller the resistance, the faster the charge transfer at the electrode–electrolyte interface, and hence the better the catalytic activity. Solution resistance ( $R_s$ ) for  $\text{WO}_3$ ,  $\text{WO}_3@\text{Nb}_2\text{C}1$ ,  $\text{WO}_3@\text{Nb}_2\text{C}2$ , and  $\text{WO}_3@\text{Nb}_2\text{C}3$  were calculated to be  $29.63 \Omega$ ,  $24.89 \Omega$ ,  $22.99 \Omega$ , and  $21.05 \Omega$ , respectively.  $R_{ct}$  values for  $\text{WO}_3$ ,  $\text{WO}_3@\text{Nb}_2\text{C}1$ ,  $\text{WO}_3@\text{Nb}_2\text{C}2$ , and  $\text{WO}_3@\text{Nb}_2\text{C}3$  were determined to be  $665 \Omega$ ,  $589 \Omega$ ,  $416 \Omega$ , and  $309 \Omega$ , respectively. The interaction of  $\text{Nb}_2\text{CT}_x$  with  $\text{WO}_3$  decreases charge transfer resistance by facilitating electron transfer and reducing electron–hole recombination, thereby providing better PEC-OER activity.

Chopped light LSV was performed with a mechanical chopper at an interval of 5 seconds, alternating light ON and light OFF. In PEC water oxidation, chopped light LSV can help optimize photoelectrodes because it provides information about light harvesting efficiency, generation of photocurrents, and the dynamics of charge carriers of the catalyst.  $\text{WO}_3@\text{Nb}_2\text{C}3$  outperformed the bare  $\text{WO}_3$  in chopped light LSV (Fig. 7c). These results agree with the LSV as well.  $\text{WO}_3@\text{Nb}_2\text{C}3$  attained a higher photocurrent. This shows that the addition of  $\text{Nb}_2\text{CT}_x$  MXene to  $\text{WO}_3$  helps in better charge separation, and it has reduced the electron–hole recombination as well; therefore, a higher photocurrent can be observed for the  $\text{WO}_3@\text{Nb}_2\text{C}3$  heterojunction. The difference in the dark current when the light is OFF and the photocurrent when the light is ON is of crucial importance in evaluating the efficiency of the catalyst for the evolution of oxygen through the oxidation of water. As depicted in Fig. 6c, we can observe that the current drops to zero when there is no light and rises swiftly when the light is ON. This indicates that the reaction is mainly driven by the photo-induced charge carriers and not through the applied voltage. Chopped light LSV can also provide insights to determine the photostability of the catalyst when the catalyst is consecutively exposed to light for up to many cycles. We performed 50 consecutive chopped light LSVs to evaluate the photostability of





**Fig. 7** PEC activities of pure  $\text{WO}_3$  and  $\text{WO}_3/\text{Nb}_2\text{CT}_x$  in 0.5 M  $\text{Na}_2\text{SO}_4$ : (a) LSV curves, (b) Nyquist plots, (c) chopped light LSV curves, (d) chopped light LSV curves for cyclic stability for  $\text{WO}_3$ , (e) chopped light LSV curves for cyclic stability for  $\text{WO}_3/\text{Nb}_2\text{C3}$  composite, (f) double layer capacitance plots for  $\text{WO}_3/\text{Nb}_2\text{C3}$  composite, (g) Mott–Schottky plots for  $\text{WO}_3$  and  $\text{WO}_3/\text{Nb}_2\text{C3}$  composite, and (h) charge carrier generation/separation and participation in water splitting.

our catalysts, and the comparison of the 10th, 20th, 30th, 40th, and 50th LSV is shown in Fig. 7d and e.  $\text{WO}_3/\text{Nb}_2\text{C3}$  outperformed  $\text{WO}_3$ . This indicates that the  $\text{WO}_3/\text{Nb}_2\text{C3}$

heterojunction has prevented degradation and photo corrosion. These results are considerable for analyzing the long-term stability of catalysts under real operating parameters.

Double layer capacitance ( $C_{dl}$ ) was determined for  $\text{WO}_3$  and  $\text{WO}_3@\text{Nb}_2\text{C}3$  by taking multiple CV cycles in non-faradaic potential range at various scan rates of 20, 40, 60, 80, and 100  $\text{mV s}^{-1}$  under dark conditions to study the intrinsic electrochemical behavior of the prepared catalysts without considering the activity induced by light (Fig. S4†).  $\Delta j$  was plotted against the scan rate, and the slope of this plot gave the  $C_{dl}$  value.  $\text{WO}_3@\text{Nb}_2\text{C}3$  exhibited a higher  $C_{dl}$  value (2.01 mF) than  $\text{WO}_3$  (1.21 mF). ECSA is directly proportional to  $C_{dl}$  value (Fig. 7f). The higher the  $C_{dl}$  value, the higher the ECSA. ECSA is determined using the following formula:  $C_{dl}/C_s$ , where  $C_s$  is the specific capacitance value of the electrode material.  $\text{WO}_3@\text{Nb}_2\text{C}3$  possessed a higher ECSA value ( $40.2 \text{ cm}^2$ ) than pristine  $\text{WO}_3$  ( $24.2 \text{ cm}^2$ ). A higher value of ECSA for  $\text{WO}_3@\text{Nb}_2\text{C}3$  indicates that there are more catalytic sites available on it compared to  $\text{WO}_3$  and larger surface area availability for charge transfer and charge accumulation.

Mott–Schottky (MS) analysis was conducted for  $\text{WO}_3$  and  $\text{WO}_3@\text{Nb}_2\text{C}3$  heterojunction in the dark to determine the flat band potential value  $V_{fb}$  and donor density  $N_d$ . The Mott–Schottky equation is given below:<sup>49,50</sup>

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 A^2 e N_d} \left( V - V_{fb} - \frac{k_B T}{e} \right)$$

where  $C$  is the differential capacitance with respect to potential,  $\varepsilon$  is the dielectric constant of the semiconductor,  $\varepsilon_0$  is the vacuum permittivity,  $A$  is the area of the electrode that is coated,  $e$  is the elementary charge,  $V$  is the applied potential,  $V_{fb}$  is the flat band potential,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature. Following heterojunction formation, the slopes of the Mott–Schottky plot within the linear region exhibit a significant decline, indicating an increase in  $N_d$ . The flat band potential of a semiconductor film can be determined from the  $x$ -intercept of the tangent line on the potential axis in a liquid junction.<sup>26,28</sup> Fig. 6g shows a positive slope, which clearly indicates n-type semiconductors.  $V_{fb}$  for  $\text{WO}_3@\text{Nb}_2\text{C}3$  is lower than that of  $\text{WO}_3$ , the donor density for  $\text{WO}_3$  is  $0.2715 \times 10^{16} \text{ cm}^{-3}$ , and  $\text{WO}_3@\text{Nb}_2\text{C}3$  possesses a higher donor density of  $0.36 \times 10^{18} \text{ cm}^{-3}$ . Higher donor density and lower flat band potential confirmed that the incorporation of  $\text{Nb}_2\text{CT}_x$  to  $\text{WO}_3$  increased charge separation, hence providing better photocatalytic activity. As depicted in Fig. 7g, it can be observed that the intercepts of MS plots reveal that a cathodic shift occurs in the  $V_{fb}$  values owing to the composite formation from 0.51 V to 0.46 V for  $\text{WO}_3$  and  $\text{WO}_3@\text{Nb}_2\text{C}3$ , respectively. For an n-type semiconductor material, compared to the conduction band value, the flat band potential is supposed to be located at a more positive potential, so the conduction band value will be  $\sim 0.1 \text{ eV}$  lower than the flat band potential value.<sup>51</sup> Therefore, the values for conduction band edge positions of  $\text{WO}_3$  and  $\text{WO}_3@\text{Nb}_2\text{C}3$  were calculated to be 0.41 and 0.36 eV, respectively. The overall band edge positions with respect to water splitting potentials were plotted by combining the band gap energy value, as shown in Fig. 7h. ESI Table 1† shows a comparison of various catalysts for photoelectrochemical water splitting in terms of the photocurrent and electrolyte used, and it is evident that the

current study shows overall superior activity compared to previous studies.

## Conclusion

In this work, composites of  $\text{WO}_3$  with  $\text{Nb}_2\text{CT}_x$  MXene were successfully synthesized by applying a hydrothermal and ultrasonic approach to develop a 2D/2D  $\text{WO}_3@\text{Nb}_2\text{CT}_x$  heterojunction. The prepared catalysts were characterized by XRD, XPS, FESEM, EDX, TEM, and UV-visible spectroscopy and photoelectrochemical measurements. The photocatalytic activity of  $\text{WO}_3$  was aimed to be enhanced by developing a heterojunction with  $\text{Nb}_2\text{CT}_x$  MXene.  $\text{Nb}_2\text{CT}_x$  is a conductive material and acts as a cocatalyst. Therefore, the composite  $\text{WO}_3@\text{Nb}_2\text{C}3$  results in improved charge transfer and lower electron–hole recombination, which is the most common limitation of any photocatalyst.  $\text{WO}_3@\text{Nb}_2\text{C}3$  showed a photocurrent density of  $4.71 \text{ mA cm}^{-2}$  at  $1.23 \text{ V}$  vs. RHE. The heterojunction  $\text{WO}_3@\text{Nb}_2\text{C}3$  showed enhanced photostability, lower charge transfer resistance, lower band gap (2.56 eV), lower  $V_{fb}$  and higher  $C_{dl}$  value (2.1 mF).  $\text{Nb}_2\text{CT}_x$  serves as a conductive bridge, which facilitates electron transport from  $\text{WO}_3$  to the external circuit, thereby minimizing energy loss and increasing the availability of electrons for water oxidation. Its integration enhances the photocatalytic behavior of  $\text{WO}_3$  by improving stability, durability, and visible light absorption while offering protection against corrosion during the oxidation process. Additionally,  $\text{Nb}_2\text{CT}_x$  optimizes charge transfer, increases catalytic sites, and expands surface area, demonstrating the synergistic effect of the heterojunction in advancing photoelectrochemical water oxidation. This study highlights a promising pathway for developing stable and sustainable photocatalysts for solar-driven green energy production.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors are grateful to the Pakistan Science Foundation for financial assistance under project no. PSF-NSFC-IV/Chem/C-QAU (27), and M. M. would like to thank the Higher Education Commission of Pakistan for indigenous PhD fellowship.

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