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# Iron/vanadium co-doped tungsten oxide nanostructures anchored on graphitic carbon nitride sheets (FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>) as a cost-effective novel electrode material for advanced supercapacitor applications

 Sajida Parveen,<sup>a</sup> Eric W. Cochran,<sup>b</sup> Sonia Zulfiqar,<sup>bc</sup> Mohammed A. Amin,<sup>d</sup> Muhammad Farooq Warsi<sup>id</sup>\*<sup>a</sup> and Khadija Chaudhary<sup>\*a</sup>

In this work, we studied the effect of iron (Fe) and vanadium (V) co-doping (Fe/V), and graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) on the performance of tungsten oxide (WO<sub>3</sub>) based electrodes for supercapacitor applications. The lone pair of electrons on nitrogen can improve the surface polarity of the g-C<sub>3</sub>N<sub>4</sub> electrode material, which may results in multiple binding sites on the surface of electrode for interaction with electrolyte ions. As electrolyte ions interact with g-C<sub>3</sub>N<sub>4</sub>, they quickly become entangled with FeV-WO<sub>3</sub> nanostructures, and the contact between the electrolyte and the working electrode is strengthened. Herein, FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> is fabricated by a wet chemical approach along with pure WO<sub>3</sub> and FeV-WO<sub>3</sub>. All of the prepared samples *i.e.*, WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> were characterized by XRD, FTIR, EDS, FESEM, XPS, Raman, and BET techniques. Electrochemical performance is evaluated by cyclic voltammetry (CV), galvanic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS). It is concluded from electrochemical studies that FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> exhibits the highest electrochemical performance with specific capacitance of 1033.68 F g<sup>-1</sup> at scan rate 5 mV s<sup>-1</sup> in the potential window range from -0.8 to 0.25 V, that is greater than that for WO<sub>3</sub> (422.76 F g<sup>-1</sup>) and FeV-WO<sub>3</sub> (669.76 F g<sup>-1</sup>). FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> has the highest discharge time (867 s) that shows it has greater storage capacity, and its coulombic efficiency is 96.7%, which is greater than that for WO<sub>3</sub> (80.1%) and FeV-WO<sub>3</sub> (92.1%), respectively. Furthermore, excellent stability up to 2000 cycles is observed in FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>. It is revealed from EIS measurements that equivalent series resistance and charge transfer values calculated for FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> are 1.82 Ω and 0.65 Ω, respectively.

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## 1. Introduction

The indiscriminate use of non-renewable resources of energy such as coal, oil, and natural gas, *etc.* for the generation of power causes environmental issues like climate change and depletion of fossil fuels. Furthermore, the planet's population is expanding quickly, and also their social desire to speed up the energy-generation and storage processes even more.<sup>1,2</sup> In view of this scenario, extensive work is being done on environment friendly and renewable technologies for energy storage to limit

the use of traditional energy resources and reduce environmental pollution.<sup>3-5</sup> Different energy storage technologies, such as lithium-ion batteries (LIBs), capacitors, supercapacitors, and other energy storage devices are commonly available to fulfill market requirements. LIBs are excellent electrochemical devices because of their large energy density,<sup>6</sup> however, they have low energy output and short lifespan because of the thick and heavy electrodes, and poor electron transfer.<sup>7</sup>

Supercapacitors as energy storage devices are classified into different categories, as electrical double layer capacitors (EDLCs), pseudo-capacitors, and hybrid capacitors. Pseudo-capacitors have higher capacitance values than EDLCs. Supercapacitors with efficient power density and higher sustainability are highly recommended for electric and hybrid vehicles as well as for electronics and backup energy systems.<sup>8-10</sup> Although supercapacitors are ideal for purposes that need relatively efficient improvements of power, such as power supply in exigent circumstances and peak power output that assists batteries in electric and hybrid vehicles, the energy storage characteristics

<sup>a</sup>Institute of Chemistry, Baghdad-ul-Jadeed Campus, The Islamia University of Bahawalpur, Bahawalpur 63100, Pakistan. E-mail: farooq.warsi@iub.edu.pk; khadija.chaudhary.kc@gmail.com

<sup>b</sup>Department of Chemical and Biological Engineering, Iowa State University, Sweeney Hall, 618 Bissell Road, Ames, Iowa 50011, USA

<sup>c</sup>Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, Ostrava 701 03, Czech Republic

<sup>d</sup>Department of Chemistry, College of Science, Taif University, PO Box 11099, Taif 21944, Saudi Arabia



of supercapacitors still need improvement.<sup>11</sup> Many of the transition metal oxides have been used as electrode material for supercapacitors, such as MoO<sub>3</sub>,<sup>12</sup> ZnO,<sup>13</sup> MnO<sub>2</sub>,<sup>14</sup> NiO,<sup>15</sup> Co<sub>3</sub>O<sub>4</sub>,<sup>16</sup> V<sub>2</sub>O<sub>5</sub>,<sup>17</sup> CuO,<sup>18</sup> NiS,<sup>19</sup> and CoS<sup>20</sup> due to pseudo-capacitive behavior. These days, the majority of researchers in this field are working on improving the electrode durability and specific capacitance. The nature of the electrode material determines a supercapacitor's entire electrochemical behavior and the electrodes with organized morphology are capable of achieving high capacitance value.<sup>21–26</sup>

Supercapacitors based on WO<sub>3</sub> have been thoroughly explored and frequently reported.<sup>27–29</sup> WO<sub>3</sub> demonstrates pseudo-capacitive behavior due to its various oxidation states, quick surface interactions, and favorable crystalline structure for the interactions with electrolyte ions. It has lately gained attention as a potential electrode material in the fabrication of pseudo-capacitors due to its outstanding capacitive performance and natural availability.<sup>30–33</sup> Additionally, WO<sub>3</sub> is known to be a potential contender for electro-catalytic performance,<sup>34</sup> in gas sensors,<sup>35</sup> electro-chromism,<sup>36</sup> rechargeable LIBs,<sup>37</sup> dye sensitized solar cells,<sup>38</sup> and for energy storage. The prime choice for supercapacitors is that the active material should have high electrical conductance and be capable of providing excellent electrical performance. Hence, multiple attempts have been made to improve WO<sub>3</sub> efficiency.

Several researchers have worked on different strategies to improve the properties of WO<sub>3</sub>. WO<sub>3</sub> has been doped with various types of metals to enhance its efficiency as a photoactive material in photoelectrochemical water splitting mechanism.<sup>39–43</sup> Further, the energy storage characteristics of WO<sub>3</sub> can also be improved by doping with different transition metal elements. For instance, Gupta *et al.* used a hydrothermal technique to synthesize Pd@WO<sub>3</sub> nanostructures with enhanced energy density for energy storage applications.<sup>44</sup> Kumar *et al.* manufactured Ni@WO<sub>3</sub> and NiWO<sub>4</sub> nanostructures by a microwave method for supercapacitor applications.<sup>45</sup> VWO<sub>3</sub> electrodes have drawn more interest.<sup>46–49</sup> In general, it has been demonstrated that increasing the energy and power density of W containing cathode layers through the doping of ecologically favorable and sustainable V elements is an effective strategy.<sup>49</sup> Further, compositing WO<sub>3</sub> with other metal oxides or carbon supports is another strategy to improve its performance. The selection of components for the manufacturing of composite depends on how efficiently they work together. In comparison to metal oxides, carbon materials usually have high conductivity, specific energy, and surface area. Therefore, active material can be deposited on highly conductive materials such as CNTs, graphene, and graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) to increase the electrical conductivity of the bare samples. The nitrogen element of g-C<sub>3</sub>N<sub>4</sub> renders it suitable for supercapacitor and battery uses.<sup>50</sup> The lone pair of electrons on nitrogen improves the surface polarity of g-C<sub>3</sub>N<sub>4</sub> based electrode material, resulting in multiple binding sites on the electrode surface, which in turn enhances the wettability and affinity of electrode material for electrolyte ions. In addition, enhancement in surface area after the addition of carbon-based g-C<sub>3</sub>N<sub>4</sub> helps in better dispersion of active sites or

improves the electroactive surface area for charge storage. Metal oxides with a pseudo-capacitive nature can be effectively integrated with g-C<sub>3</sub>N<sub>4</sub> structure in order to enhance the electrochemical performance of the subsequent electrode material.<sup>50–54</sup>

Hence, in this work, we first time report the influence of Fe and V co-doping and g-C<sub>3</sub>N<sub>4</sub> fabrication on the structural, functional, morphological, and electrochemical performance of the WO<sub>3</sub> for supercapacitor study. WO<sub>3</sub> and FeV-WO<sub>3</sub> were synthesized by co-precipitation method and its composite with (g-C<sub>3</sub>N<sub>4</sub>) was successfully fabricated by ultra-sonication technique. The electrochemical efficiency of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> was compared with pure WO<sub>3</sub> and FeV-WO<sub>3</sub>, and prepared samples were analyzed by different characterization techniques *i.e.* XRD, FTIR, FESEM, EDS, XPS, Raman, and BET analysis. The electrochemical measurements were also carried out by CV, GCD, and EIS measurements.

## 2. Experimental part

### 2.1. Materials

Sodium tungstate (Na<sub>2</sub>WO<sub>4</sub>), ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>), hydrochloric acid (HCl), ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>), iron(III) nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), sodium carboxy methyl cellulose (SCMC), and ethanol (C<sub>2</sub>H<sub>6</sub>O) were used. The chemicals were pure and used without further purification.

### 2.2. Synthesis of FeV-WO<sub>3</sub>

Iron vanadium co-doped tungsten oxide (FeV-WO<sub>3</sub>) was prepared by adding 0.2 g of ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>), 0.2 g of iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>), and 2 g of sodium tungstate (Na<sub>2</sub>WO<sub>4</sub>) into the mixture of water and ethylene glycol (volumetric ratio of 1 : 2). Obtained solution was stirred at 75 °C for almost 10 min along with continuous addition of 10 mL conc. HCl until pH ~ 2 was achieved. After that, reaction was allowed to age for 12 h. Precipitates were washed with distilled water and ethanol successively until it became neutral. Then, the brown green colored FeV-WO<sub>3</sub> precipitates were dried in the electric oven at 85 °C. Next, dried precipitates were annealed at 250 °C for 3 h and ground well to fine powder. In addition, pure WO<sub>3</sub> was also synthesized for comparison following the same methodology without adding NH<sub>4</sub>VO<sub>3</sub> and Fe (NO<sub>3</sub>)<sub>3</sub> during the first step.

### 2.3. Synthesis of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>)

Appropriate amount of melamine was taken in a ceramic crucible and placed in the lab furnace for annealing at 500 °C for 2 h. The yellow-colored powder obtained was allowed to cool down and then ground in to fine powder. For exfoliation, as obtained powdered material was added in water and ultra-sonicated for 5 h and then dried in the electric oven. Hence, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was obtained. It was used for the synthesis of the composite.

### 2.4. Synthesis of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>

The composite of FeV-WO<sub>3</sub> was prepared with g-C<sub>3</sub>N<sub>4</sub> through ultra-sonication method. Briefly, FeV-WO<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> were



taken in 8:2 ratio in 20 mL distilled water. After ultrasonication of the solution for 2 h, the homogeneous suspension was dried in the electric oven at 60 °C. Finally, brown yellow colored powder of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> was obtained.

### 2.5. Electrochemical tests

All the electrochemical measurements *i.e.*, GCD, CV, and EIS were performed with the GAMRY interface/5000E consisting of three electrodes with 1 M Na<sub>2</sub>SO<sub>4</sub> as an electrolyte. Platinum wire and Ag/AgCl were utilized as counter and reference electrodes. For working electrode, 0.005 g of the prepared samples were added into 3 μL of sodium carboxy methyl cellulose (SCMC) and then 1 mL of ethanol was added into it. Nickel foam was cut into a piece of 2 cm in length and 1 cm in width, washed with HCl, and dried in oven at 60 °C. The mixture for working electrode was loaded on Ni foam and dried at 60 °C. The whole synthesis process and fabrication of electrode are schematically shown in Fig. 1.

## 3. Results and discussion

### 3.1. Phase analysis

The structural analysis of as fabricated samples *i.e.*, WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> was performed by X-ray diffraction technique, as shown in Fig. 2(a). XRD pattern of WO<sub>3</sub> showed peaks at  $2\theta$  values of 23.13°, 24.05°, 28.91°, 33.83°, 42.02°, 45.41°, 47.37°, 49.45°, 50.76°, 55.03°, 60.05°, 61.25°, 63.10°, 69.77°, 71.51°, 74.113°, and 76.75°, which can be assigned to (101), (201), (111), (300), (211), (002), (220), (310), (112), (221), (400), (212), (401), (222), (312), (103), and (330) diffraction planes, respectively (JCPDS# 33-1387). It confirms the monoclinic crystal phase of

WO<sub>3</sub>. High intensity of peaks showed the excellent crystalline nature of WO<sub>3</sub>.<sup>55</sup> XRD pattern of FeV-WO<sub>3</sub> is almost identical to the WO<sub>3</sub>, although there is slight peak shifting to higher  $2\theta$  values which may result from the contraction in lattice parameters after the doping of Fe and V ions in parent lattice of WO<sub>3</sub> (Fig. 2(b)). In XRD pattern of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>, an additional peak appeared at 27.2° in correspondence to (002) plane which is the distinguishable peak of g-C<sub>3</sub>N<sub>4</sub>.<sup>56</sup> It is noteworthy that the diffraction peaks of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> shifted to a lower angle as compared to FeV-WO<sub>3</sub>, with increase in the breadth of peaks (indicated by peak corresponding to (300) plane in Fig. 2(b)). This peak shifting of (300) plane can be explained in terms of changes in *d*-spacing and other crystallite parameters as a result of inclusion of g-C<sub>3</sub>N<sub>4</sub> sheets in FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> composite.<sup>57,58</sup> Appearance of (002) plane and peak shifting confirms the successful assembly of FeV-WO<sub>3</sub> with g-C<sub>3</sub>N<sub>4</sub> sheets.

### 3.2. Functional group analysis

For the functional group analysis of all the prepared samples, FTIR technique was used. FTIR spectra of all the three prepared samples *i.e.*, WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> are exhibited in Fig. 3(a)–(c) in the wavenumber range of 500–4000 cm<sup>-1</sup>. FTIR spectrum of the WO<sub>3</sub> show a broad band in the range of 500 cm<sup>-1</sup> to 1000 cm<sup>-1</sup>. In Fig. 3(a), bands in the spectrum of WO<sub>3</sub> at 644 cm<sup>-1</sup> and 925 cm<sup>-1</sup> clearly indicate the O–W–O vibrations and band that appeared at 3446 cm<sup>-1</sup> is assigned to the stretching mode of the O–H group due to the adsorbed water.<sup>59,60</sup> Similarly, in FTIR spectrum of FeV-WO<sub>3</sub> two bands appeared at 650 cm<sup>-1</sup> and 925 cm<sup>-1</sup> show O–W–O vibrational modes (Fig. 3(b)).<sup>61</sup> The band at 3626 cm<sup>-1</sup> is due to the stretching vibration of O–H.<sup>62</sup> In the FTIR spectrum of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>, various bands are shown

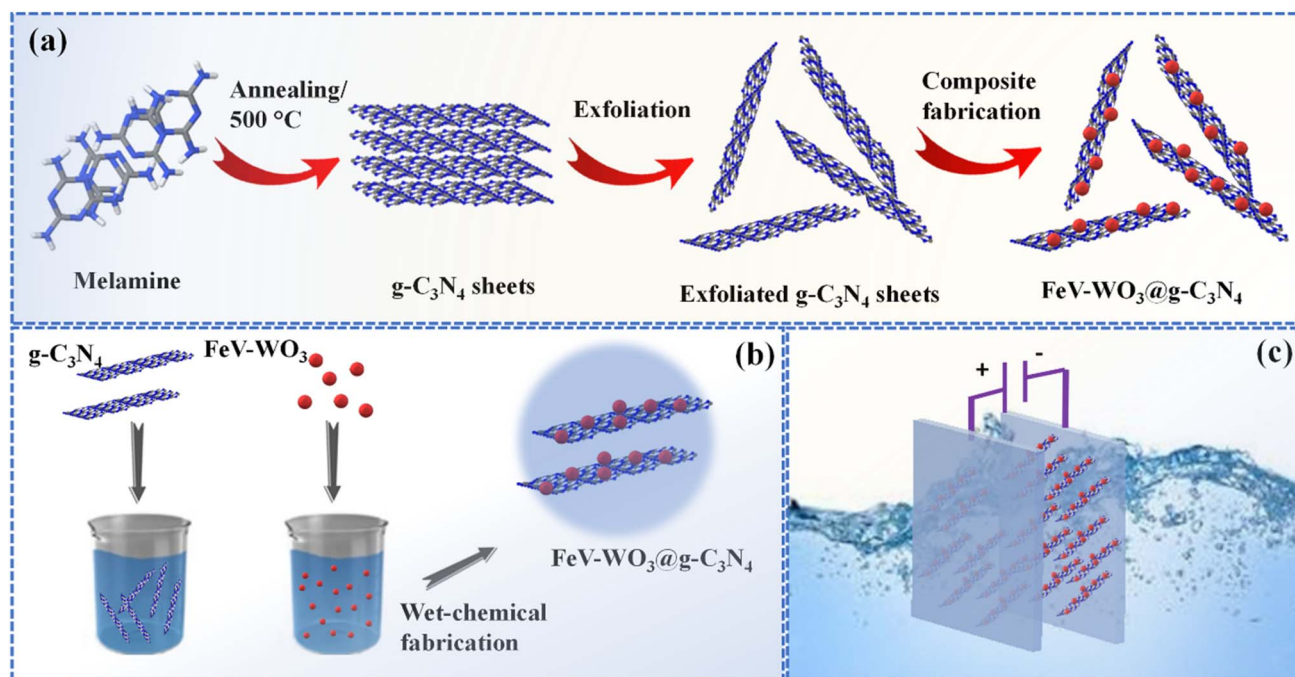


Fig. 1 Schematic representation of (a and b) synthesis of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> composite and (c) fabrication of electrode.



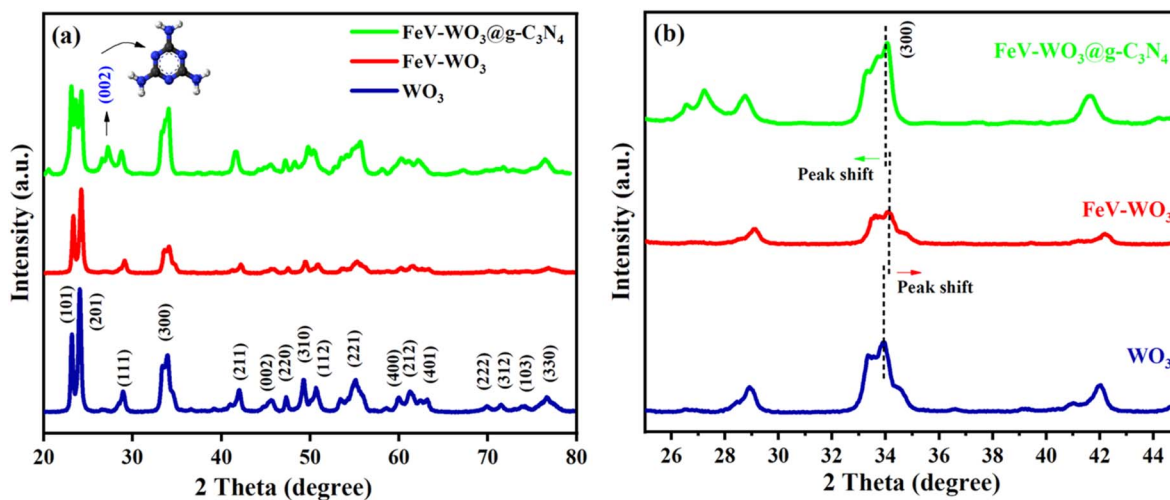


Fig. 2 (a) XRD patterns of prepared WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> composite, and (b) peak shift in XRD peaks of WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> composite.

in the region of 500–1632 cm<sup>-1</sup> (Fig. 3(c)).<sup>63</sup> Bands that appeared at 631 cm<sup>-1</sup>, and 937 cm<sup>-1</sup> indicate the O–W–O vibrational modes. The bands at 1237 cm<sup>-1</sup>, 1320 cm<sup>-1</sup>, and 1421 cm<sup>-1</sup>

demonstrate different vibrational modes from g-C<sub>3</sub>N<sub>4</sub> ring. The band that emerged at 3620 cm<sup>-1</sup> is attributed to O–H stretching vibration.<sup>64</sup>

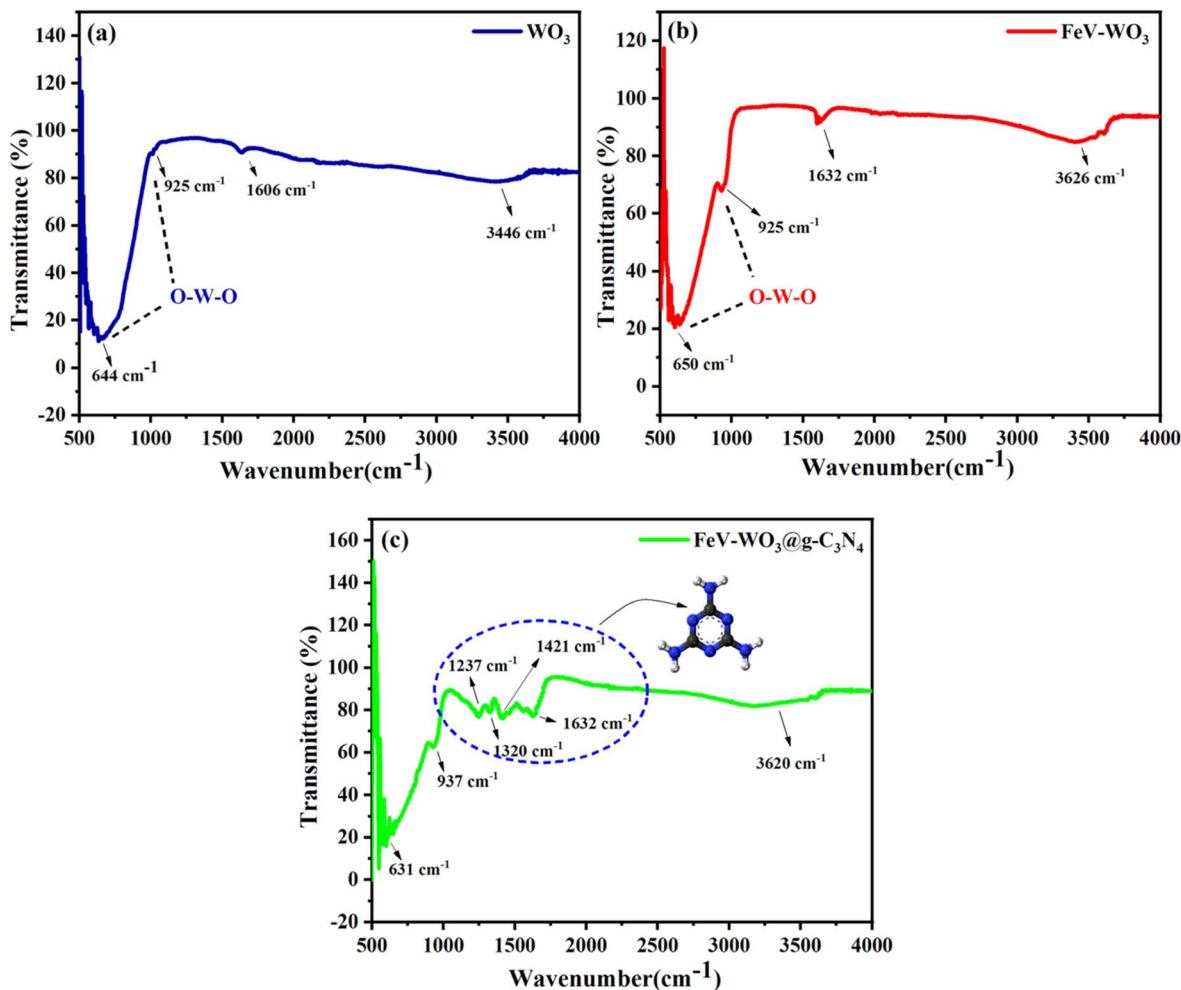


Fig. 3 FTIR spectra of (a) WO<sub>3</sub>, (b) FeV-WO<sub>3</sub>, and (c) FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> composite.



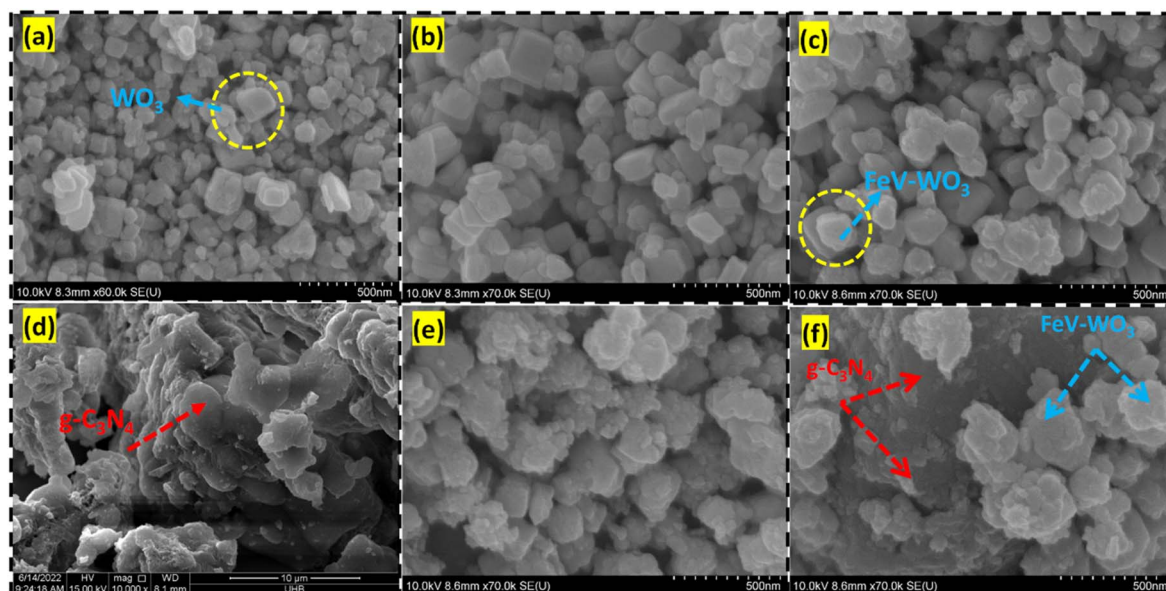


Fig. 4 FESEM images of (a and b)  $\text{WO}_3$ , (c)  $\text{FeV-WO}_3$ , (d)  $\text{g-C}_3\text{N}_4$ , and (e and f)  $\text{FeV-WO}_3@ \text{g-C}_3\text{N}_4$  composite.

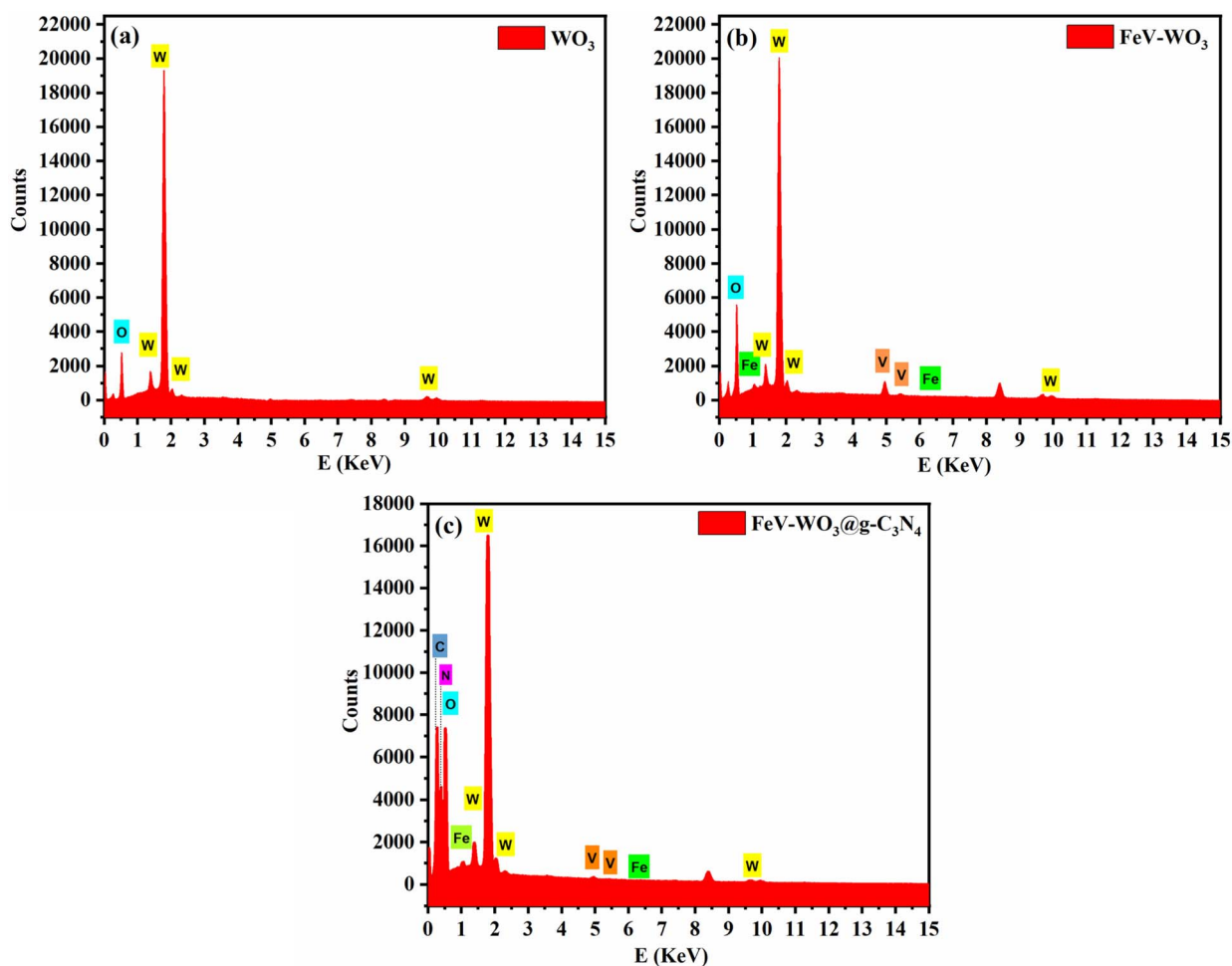


Fig. 5 EDS spectra of (a)  $\text{WO}_3$ , (b)  $\text{FeV-WO}_3$ , and (c)  $\text{FeV-WO}_3@ \text{g-C}_3\text{N}_4$  composite.



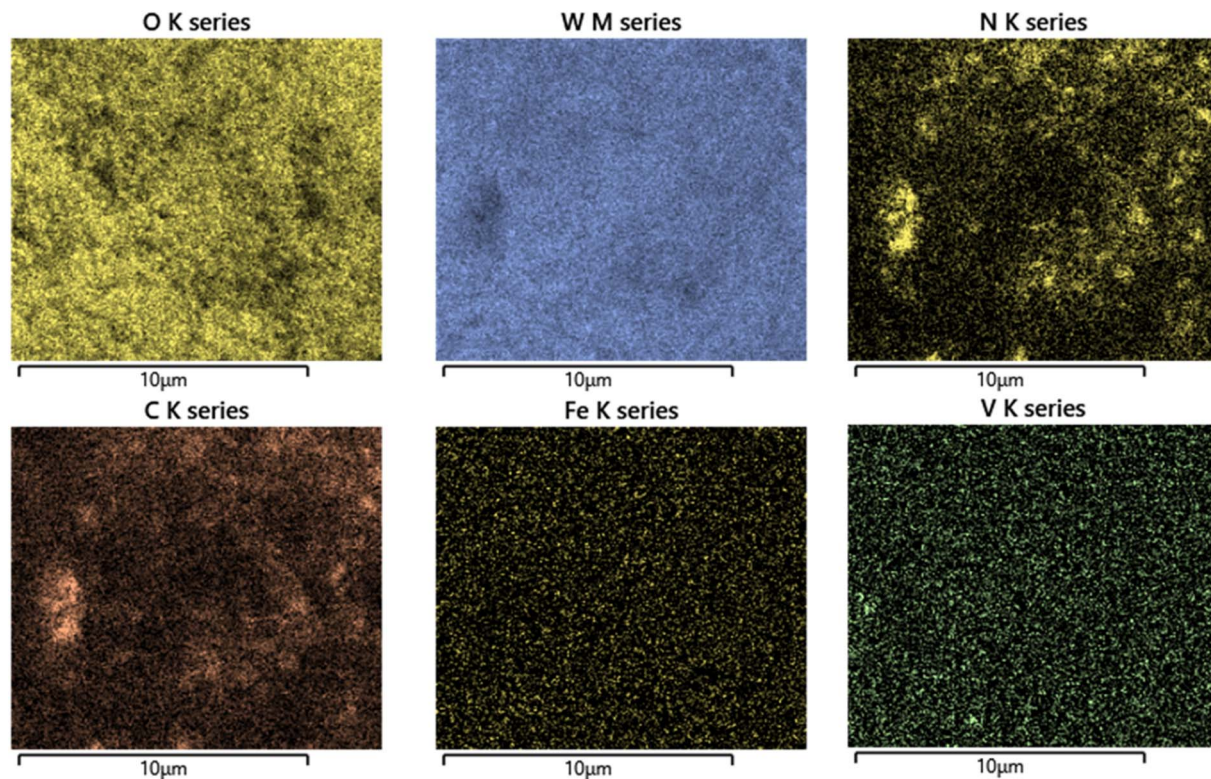
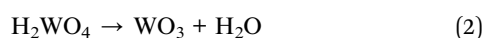


Fig. 6 EDS mapping of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> for O, W, N, C, Fe, and V.

### 3.3. Morphological analysis

The apparent shape, particle size distribution, texture, and dimensional nature of the produced nanostructures and composite were examined by FESEM analysis. FESEM images of the prepared samples are shown in Fig. 4(a)–(f). Fig. 4(a) and (b) exhibits the FESEM micrographs of WO<sub>3</sub> that shows asymmetrical 3D nanostructures with inhomogeneous particle sizes. The formation of asymmetric WO<sub>3</sub> nanostructures in the acidic medium can be explained with the help of the following eqn (1) and (2):<sup>65</sup>



In the acidic medium, H<sup>+</sup> and WO<sub>4</sub><sup>−2</sup> combine to form H<sub>2</sub>WO<sub>4</sub>. Nucleation and crystal growth largely depends on the reaction conditions *i.e.*, pH, temperature, and reaction time.<sup>66,67</sup> At low pH (high concentration of H<sup>+</sup> ions) a large number of H<sub>2</sub>WO<sub>4</sub> are formed. Supersaturation of H<sub>2</sub>WO<sub>4</sub> is the driving force for nucleation.<sup>68</sup> At supersaturation, when the decomposition temperature is attained, H<sub>2</sub>WO<sub>4</sub> degrades to several small 0D WO<sub>3</sub> nanoparticles. As the reaction time increases, these small nuclei in the absence of any surfactant aggregate together and grow into irregular shaped or asymmetric nanostructures.<sup>69</sup> FESEM image of FeV-WO<sub>3</sub> is represented in Fig. 4(c), which shows not much different morphology from WO<sub>3</sub>. FESEM image of g-C<sub>3</sub>N<sub>4</sub> depicted in Fig. 4(d) clearly shows that g-C<sub>3</sub>N<sub>4</sub> is

comprised of sheet like structure with irregular surface that increases the surface area of the material. Fig. 4(e) and (f) for FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> shows that FeV-WO<sub>3</sub> nanostructures were dispersed on the surface of g-C<sub>3</sub>N<sub>4</sub> sheets. The particles of FeV-WO<sub>3</sub> can easily attach to the surface of g-C<sub>3</sub>N<sub>4</sub> due to the rough and uneven surface of g-C<sub>3</sub>N<sub>4</sub>. Such structures enhance the specific surface area that discloses more active sites and is more favorable for transfer of charges.<sup>70</sup> It is revealed that the overall shape of the composite shows an assemblage of FeV-WO<sub>3</sub> nanostructures with a loose stack of 2D sheets of g-C<sub>3</sub>N<sub>4</sub>.

### 3.4. Elemental analysis

In Fig. 5(a)–(c) EDS spectra of WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> are shown. EDS spectrum of WO<sub>3</sub> consists of W (at *E* = 1.38 keV, 1.81 keV, and 9.6 keV) and O (0.53 keV) elements. After the doping of Fe and V ions, new peaks appeared at 0.79 keV and 6.39 keV for Fe, and 4.9 keV and 5.4 keV for V. Finally, for FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>, C and N elements were observed at 0.23 keV and 0.38 keV. EDS mapping of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> is shown in Fig. 6 which clearly represents the presence of all required elements *i.e.*, O, W, N, C, Fe, and V.

### 3.5. XPS analysis

XPS measurements were performed to further analyze the elemental composition of the prepared samples. XPS spectra of WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> are depicted in Fig. 7(a)–(d). The overall survey spectrum of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> in Fig. 7(a) confirms the presence of all elements *i.e.*, W, O,



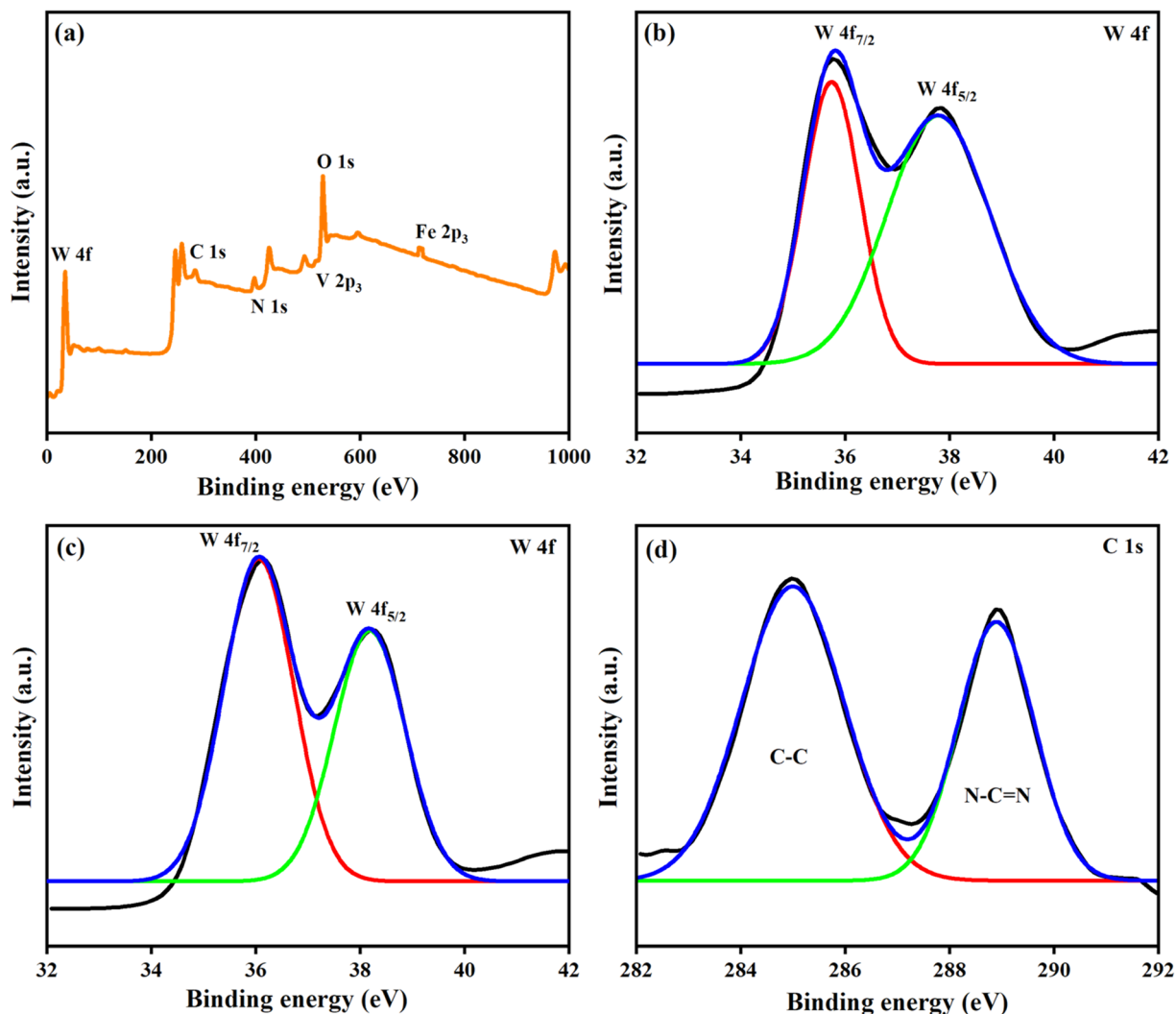


Fig. 7 (a) XPS survey spectrum of FeV- $\text{WO}_3$ @g- $\text{C}_3\text{N}_4$ . Deconvoluted high resolution XPS spectra of W 4f core levels of (b)  $\text{WO}_3$ , (c) FeV- $\text{WO}_3$ , and C 1s core levels of (d) FeV- $\text{WO}_3$ @g- $\text{C}_3\text{N}_4$ .

Fe, V, C, and N. The primary doublet peaks of  $\text{WO}_3$  at binding energies of 35.7 and 37.8 eV are possessed by W  $4f_{7/2}$  and W  $4f_{5/2}$  core levels, respectively (Fig. 7(b)).<sup>71</sup> These peaks represent that tungsten exhibits an oxidation state of  $\text{W}^{+6}$ . The difference in binding energy between the W  $4f_{7/2}$  and W  $4f_{5/2}$  levels is around 2.1 eV, which demonstrates excellent purity of  $\text{WO}_3$ . In XPS spectrum of FeV- $\text{WO}_3$  the binding energy of FeV- $\text{WO}_3$  nanoparticles was shifted slightly to lower energy side as compared to that of pure  $\text{WO}_3$ , which is attributed to the strong interaction of Fe and V with  $\text{WO}_3$  (Fig. 7(c)). The XPS spectrum of FeV- $\text{WO}_3$ @g- $\text{C}_3\text{N}_4$  confirms the presence of g- $\text{C}_3\text{N}_4$  (Fig. 7(d)). The peaks that emerged at 284.9 eV and 288.9 eV are attributed to the C-C and N-C=N bonds, respectively.<sup>72</sup>

### 3.6. Raman spectroscopy

Raman spectroscopy was used to investigate the local symmetry of the prepared materials. Raman spectra of  $\text{WO}_3$ , FeV- $\text{WO}_3$ , and FeV- $\text{WO}_3$ @g- $\text{C}_3\text{N}_4$  are exhibited in Fig. 8(a)–(c). In Fig. 8(a) peaks emerged at  $127\text{ cm}^{-1}$ ,  $260\text{ cm}^{-1}$ ,  $324\text{ cm}^{-1}$ ,  $707\text{ cm}^{-1}$ , and

$802\text{ cm}^{-1}$  in  $\text{WO}_3$  spectra confirmed that the synthesized material exhibits monoclinic phase.<sup>73</sup> It is observed that peaks emerged in two pairs from  $100\text{--}400\text{ cm}^{-1}$  and  $600\text{--}900\text{ cm}^{-1}$  corresponding to O-W-O bending and stretching modes, respectively.<sup>74</sup> The monoclinic phase  $\text{WO}_3$  exhibits a tilted and corner-shaped octahedral structure. The W atoms present on the off-center of the structure form 3 longer and 3 shorter bonds with the adjacent oxygen atom. This shows that the  $\text{WO}_3$  tungsten ion has a coordination number '6' in the prepared sample.<sup>75</sup> Raman spectra of FeV- $\text{WO}_3$  showed similar pattern with almost same peak positions as exhibited by pure  $\text{WO}_3$  (Fig. 8(b)). However, after the addition of g- $\text{C}_3\text{N}_4$ , two new peaks appeared in Fig. 8(c) at  $1358\text{ cm}^{-1}$  and  $1570\text{ cm}^{-1}$  corresponding to D and G bands of g- $\text{C}_3\text{N}_4$ .<sup>76–78</sup>

### 3.7. BET analysis

The  $\text{N}_2$  adsorption/desorption isotherms with BJH pore size distribution plot are given in Fig. 9(a) and (b) for FeV- $\text{WO}_3$ @g- $\text{C}_3\text{N}_4$ .  $\text{N}_2$  adsorption/desorption isotherms show typical type-IV





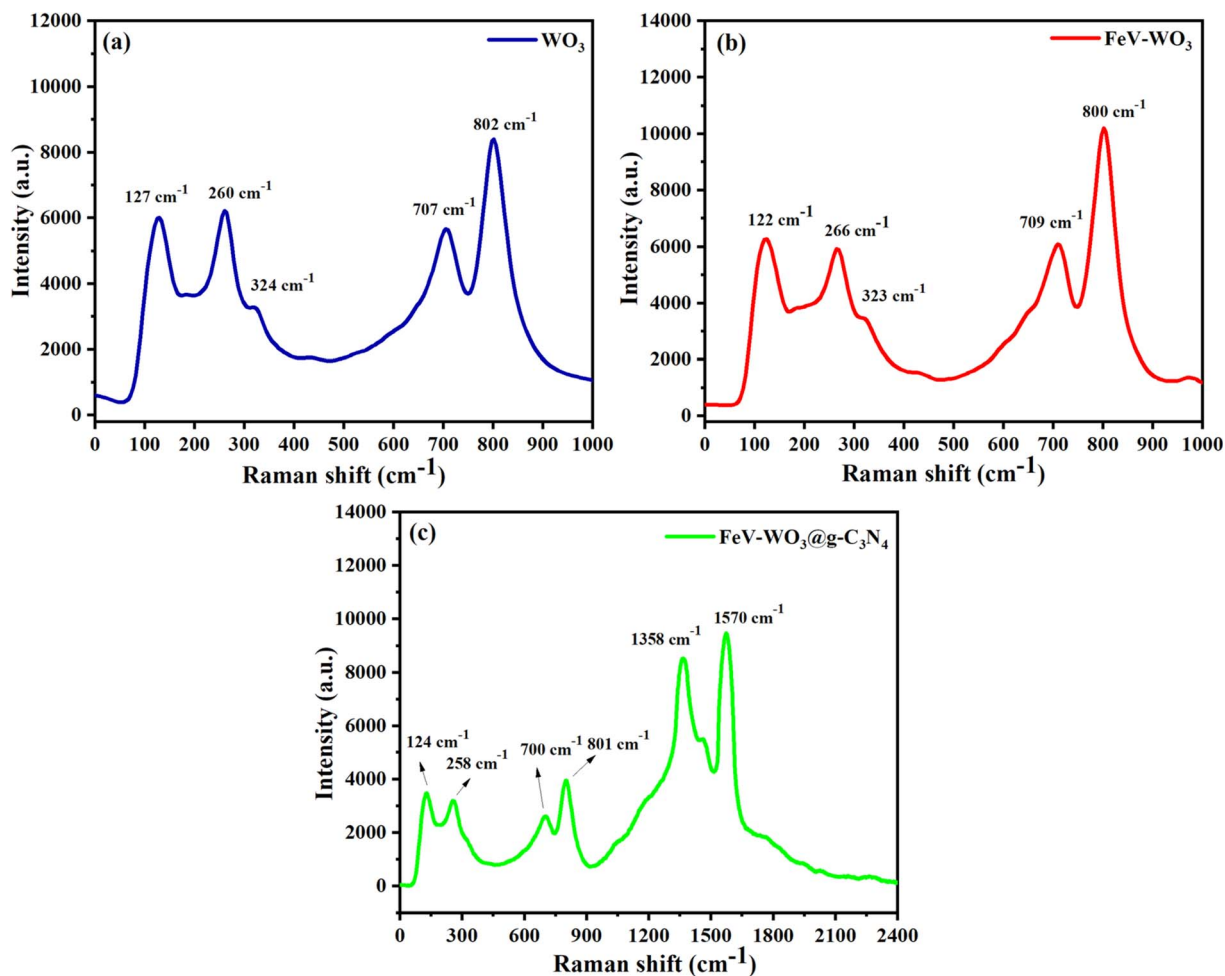


Fig. 8 Raman spectra of (a)  $\text{WO}_3$ , (b)  $\text{FeV-WO}_3$ , and (c)  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  composite.

behavior with a small  $\text{H}_3$  hysteresis loop in range of 0.8–1 (Fig. 9(a)).<sup>79</sup> Presence of  $\text{H}_3$  hysteresis loop indicates the existence of mesopores in  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  which can also be

verified from pore size distribution plot. Based on adsorption/desorption isotherms, the BET surface area for  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  was determined to be  $40.2 \text{ m}^2 \text{ g}^{-1}$ . This significant specific

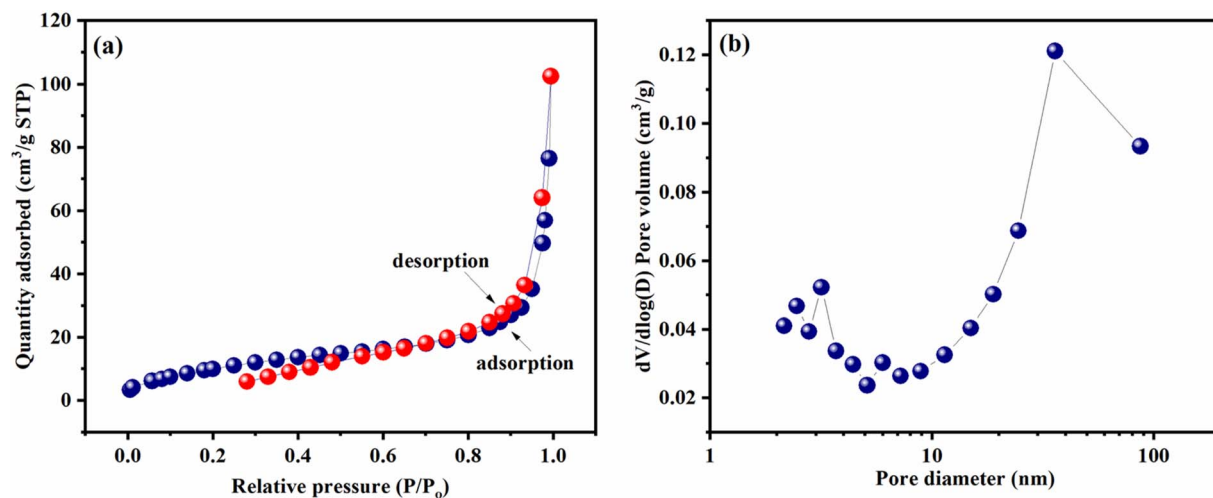


Fig. 9 (a)  $\text{N}_2$  adsorption/desorption isotherms and (b) pore size distribution plot for  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  composite.



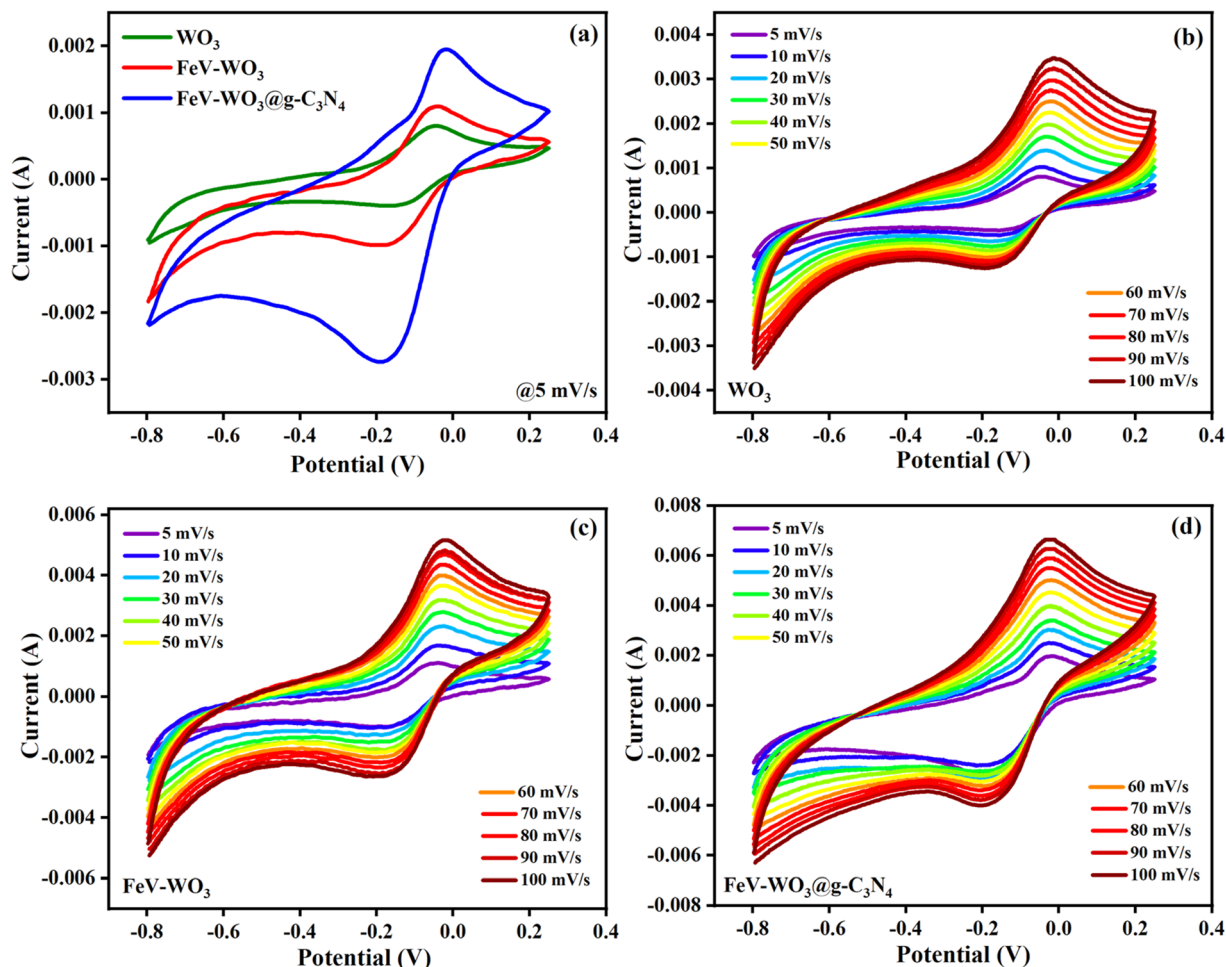


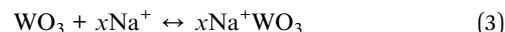
Fig. 10 CV profiles; (a) comparative CV curves of  $\text{WO}_3$ ,  $\text{FeV-WO}_3$ , and  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  taken at scan rate  $5 \text{ mV s}^{-1}$ , (b) CV curves of  $\text{WO}_3$  at 5–100  $\text{mV s}^{-1}$ , (c) CV curves of  $\text{FeV-WO}_3$  at 5–100  $\text{mV s}^{-1}$ , and (d) CV curves of  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  at 5–100  $\text{mV s}^{-1}$ .

surface area is certainly contributed by the  $g\text{-C}_3\text{N}_4$  sheets.<sup>80</sup> Pore size distribution plot in Fig. 9(b) shows that the mesopores are centralized at  $\sim 3 \text{ nm}$  and  $\sim 35 \text{ nm}$ . These mesopores in  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  develop ion diffusion channels and provide short ion diffusion paths with small resistance. The electrolyte ions can reach the interfacial sections of active electrode material through these mesopores which will lead to an enhancement of charge storage capacity of  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$ .<sup>81</sup>

## 4. Electrochemical analysis

Electrochemical properties of all the prepared samples were tested by cyclic voltammetry (CV), galvanic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) through a three electrode system in the electrolyte of 1 M  $\text{Na}_2\text{SO}_4$ . CV of  $\text{WO}_3$ ,  $\text{FeV-WO}_3$ , and  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  electrodes was performed at room temperature ( $26^\circ\text{C}$ ) at different scan rates from  $5 \text{ mV s}^{-1}$  to  $100 \text{ mV s}^{-1}$  in Fig. 10(a)–(d). The potential window range of the CV profile was from  $-0.8$  to  $0.25 \text{ V}$  (*vs.*  $\text{Ag}/\text{AgCl}$ ). Fig. 10(a) shows comparative CV profiles of all samples at  $5 \text{ mV s}^{-1}$ . The CV curves exhibited duck shape with clear oxidation and reduction peaks which shows

the pseudo-capacitive processes. During the charging process,  $\text{Na}^+$  ions from the electrolyte were successfully incorporated onto the surface of electrodes and detached during the discharging process. The whole response mechanism can be illustrated by the following reaction in eqn (3):



Further, it can be clearly observed that the composite  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  exhibited higher current and CV area as compared to  $\text{WO}_3$  and  $\text{FeV-WO}_3$  which is related to higher electrodeposition and charge storage capacity, indicating the advantages of  $g\text{-C}_3\text{N}_4$  for enhanced electrochemical performance. The current of the CV curves increased by increasing the scan rate in all cases (Fig. 10(b)–(d)) which shows direct relation between scan rate and current. CV curves remained uniform along y-axis with the increase in scan rate, and it also shows the good reversibility of redox processes.<sup>82</sup>

Specific capacitance of all the prepared electrodes at different scan rates *i.e.*,  $5 \text{ mV s}^{-1}$  to  $100 \text{ mV s}^{-1}$  was calculated by the following eqn (4):<sup>83,84</sup>



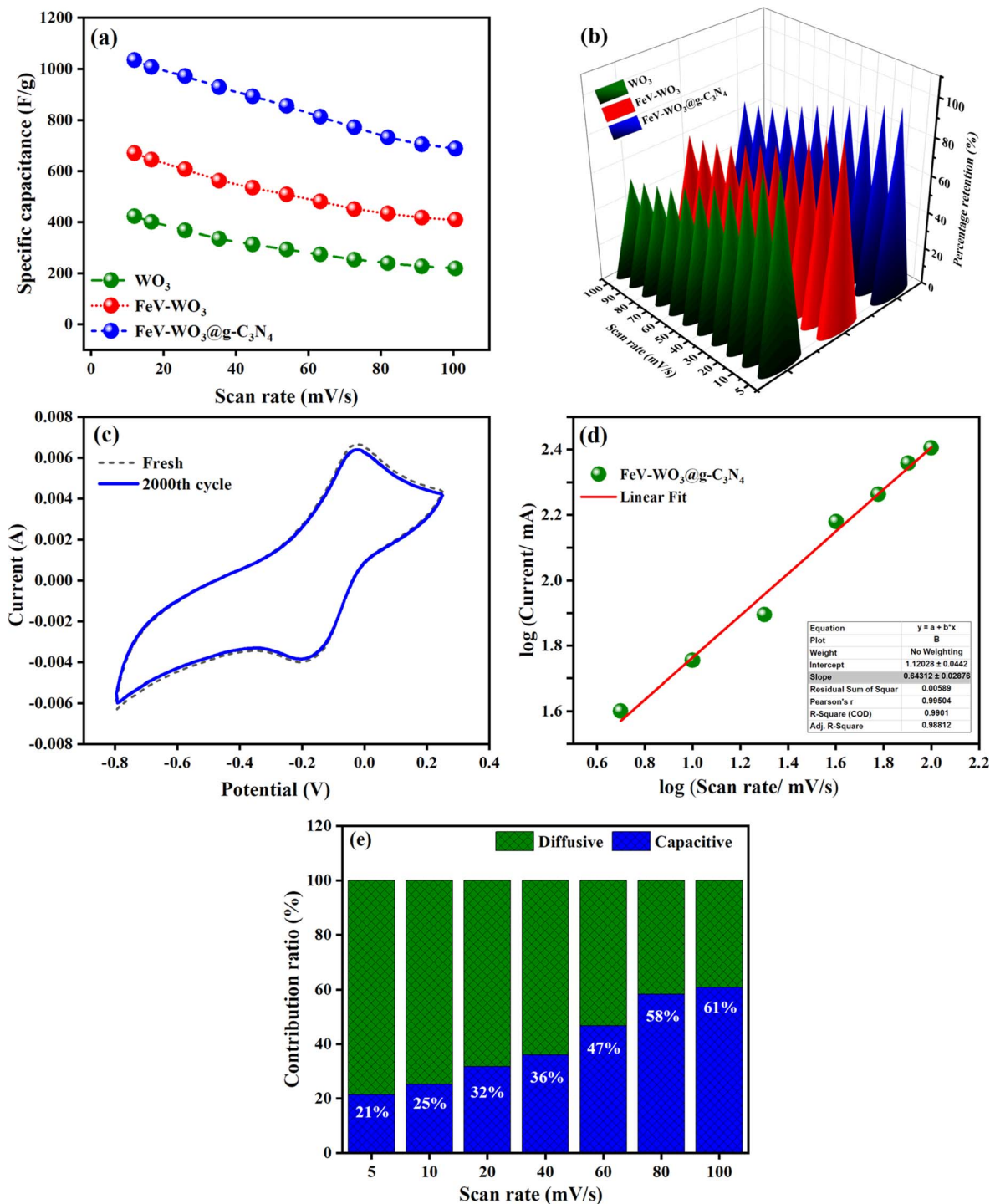


Fig. 11 (a) Specific capacitance of WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>, (b) capacitance retention of WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> at scan rates (5–100 mV s<sup>-1</sup>), (c) CV plot of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> for 2000 cycles to test stability at 100 mV s<sup>-1</sup>, (d) log (scan rate) vs. log (current) for FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>, and (e) contribution ratio for FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> at different scan rates.

$$C_{SP} = \int IdV / (2 \times m \times \Delta V) \quad (4)$$

In the above formula,  $\int IdV$  is the area of CV loop,  $m$  is the mass of material deposited on electrode, and  $\Delta V$  is applied potential limits.

The specific capacitance values calculated for WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> were found to be 422.76 F g<sup>-1</sup>, 669.76 F g<sup>-1</sup>, and 1033.68 F g<sup>-1</sup>, respectively. As expected, FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> has the highest specific capacitance value than WO<sub>3</sub> and FeV-WO<sub>3</sub> which is attributed to the increased



**Table 1** Specific capacitance of all the prepared electrodes at different scan rates

| Scan rate<br>(mV s <sup>-1</sup> ) | Specific capacitance (F g <sup>-1</sup> ) |                     |  |
|------------------------------------|---|---------------------|--|
|                                    | WO <sub>3</sub>                           | FeV-WO <sub>3</sub> | FeV-WO <sub>3</sub> @g-C <sub>3</sub> N <sub>4</sub> |
| 5                                  | 422.76                                    | 669.76              | 1033.68  |
| 10                                 | 400.38                                    | 645.06              | 1006.33  |
| 20                                 | 367.18                                    | 606.94              | 971.04   |
| 30                                 | 334.51                                    | 562.24              | 928.28   |
| 40                                 | 313.18                                    | 533.72              | 892.89   |
| 50                                 | 293.01                                    | 508.01              | 855.37   |
| 60                                 | 273.69                                    | 480.5               | 812.74   |
| 70                                 | 253.52                                    | 450.29              | 771.4  |
| 80                                 | 239.29                                    | 433.43              | 731.14   |
| 90                                 | 227.46                                    | 416.71              | 704.48   |
| 100                                | 218.96                                    | 408.43              | 687.79   |

**Table 2** Specific capacitance retention (%) for WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> at scan rate from 5–100 mV s<sup>-1</sup>

| Scan rate<br>(mV s <sup>-1</sup> ) | Specific capacitance retention (%) |                     |  |
|------------------------------------|------------------------------------|---------------------|--|
|                                    | WO <sub>3</sub>                    | FeV-WO <sub>3</sub> | FeV-WO <sub>3</sub> @g-C <sub>3</sub> N <sub>4</sub> |
| 5                                  | 100                                | 100                 | 100  |
| 10                                 | 94.7                               | 96.31               | 97.35  |
| 20                                 | 86.85                              | 90.62               | 93.94  |
| 30                                 | 79.12                              | 83.94               | 89.8   |
| 40                                 | 74.08                              | 79.68               | 86.38  |
| 50                                 | 69.31                              | 75.85               | 82.75  |
| 60                                 | 64.73                              | 71.74               | 78.62  |
| 70                                 | 59.97                              | 67.23               | 74.62  |
| 80                                 | 56.6                               | 64.71               | 70.73  |
| 90                                 | 53.8                               | 62.21               | 68.15  |
| 100                                | 51.79                              | 60.98               | 66.53  |

interactions between electrolyte solution and active sites due to the presence of g-C<sub>3</sub>N<sub>4</sub>. The electrons interact with g-C<sub>3</sub>N<sub>4</sub>, they quickly become entangled with WO<sub>3</sub> nanostructures, and the contact between the electrolyte and the working electrode is further strengthened by the structure of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> due to their synergistic effects. The morphology of the g-C<sub>3</sub>N<sub>4</sub> speeds up the charge transfer between FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> and current collector which reveals the efficient electrochemical performance of the FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>. Fig. 11(a) shows change in specific capacitance of electrode with scan rate. Specific capacitance values at different scan rates for all samples are presented in Table 1. The specific capacitance of electrodes degraded with the scan rate that is because at high scan rate the charge storage process is mostly limited to the surface of electrode due to the limited time. Capacitance retention values at different scan rates for all samples are presented in Table 2. As found, FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> has highest capacitance retention value than WO<sub>3</sub> and FeV-WO<sub>3</sub> (Fig. 11(b)). The fundamental need of a supercapacitor for its real time implementation is the long-term cycle stability. In order to test the cyclic stability of the FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>, CV measurement was repeated at constant scan rate of 100 mV s<sup>-1</sup> in 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. The

stability test of the electrode for 2000 cycles is shown in Fig. 11(c). It can be seen that our system can sustain approximately 2000 CV runs without any significant loss in the performance and distortion of CV shape. The percentage capacitance retention after 2000 cycles was determined to be 97.3%. A graph was plotted between log (scan rate) vs. log (current) for kinetic study of electrochemical measurements by Dunn's method (eqn (5) and (6)).<sup>85</sup>

$$i = av^b \quad (5)$$

Eqn (5) can be written as:

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

By linear fitting, the slope value of anodic peak was found to be 0.643, represented in Fig. 11(d). This value of slope indicates that the dominant charge storage mechanism is diffusion controlled. Fig. 11(e) shows percentage contribution to charge storage at scan rates (5 to 100 mV s<sup>-1</sup>). The bar graph clearly indicates that at high scan rates diffusion controlled processes become limited and mostly the surface of electrode takes part in charge storage process, as discussed beforehand.

The GCD plots of the prepared electrodes WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> at current density of 1 A g<sup>-1</sup> and potential range of -0.8 to 0.25 V are represented in Fig. 12(a). GCD plots integrate to form quasi-triangular shape that represents electrochemical redox reactions at the electrode-electrolyte interface. Discharge time of the prepared electrodes WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> was 440 s, 649 s, and 867 s, respectively. FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> exhibits a much longer discharge time than WO<sub>3</sub> and FeV-WO<sub>3</sub> indicating that it has greater charge storage capacity. The GCD plots of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> at different current densities *i.e.*, 1 A g<sup>-1</sup>, 3 A g<sup>-1</sup>, 5 A g<sup>-1</sup>, 7 A g<sup>-1</sup>, and 9 A g<sup>-1</sup> are represented in Fig. 12(b). GCD plots demonstrate the good symmetry of the curves with no distortion in the shape of curves at high current densities. The coulombic efficiency for all electrodes was calculated by the following eqn (7):

$$\text{Coulombic efficiency (\%)} = \frac{T_d}{T_c} \times 100 \quad (7)$$

The calculated coulombic efficiency of WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> at 1 A g<sup>-1</sup> was 80.1%, 92.1%, and 96.7%, respectively, as shown in Fig. 12(c). FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> exhibits higher value of coulombic efficiency than WO<sub>3</sub> and FeV-WO<sub>3</sub> because of the presence of g-C<sub>3</sub>N<sub>4</sub>. Generally, higher value of internal resistance disturbs the coulombic efficiency value of energy storing material by consumption of a small amount of energy during the discharge time, that's why the energy released is always less than the amount of energy stored. The greater discharge current is related to the greater redox reactions that also tend to increase the internal resistance. The best coulombic efficiency value for composite illustrates uniformed charge and discharge current values and low internal





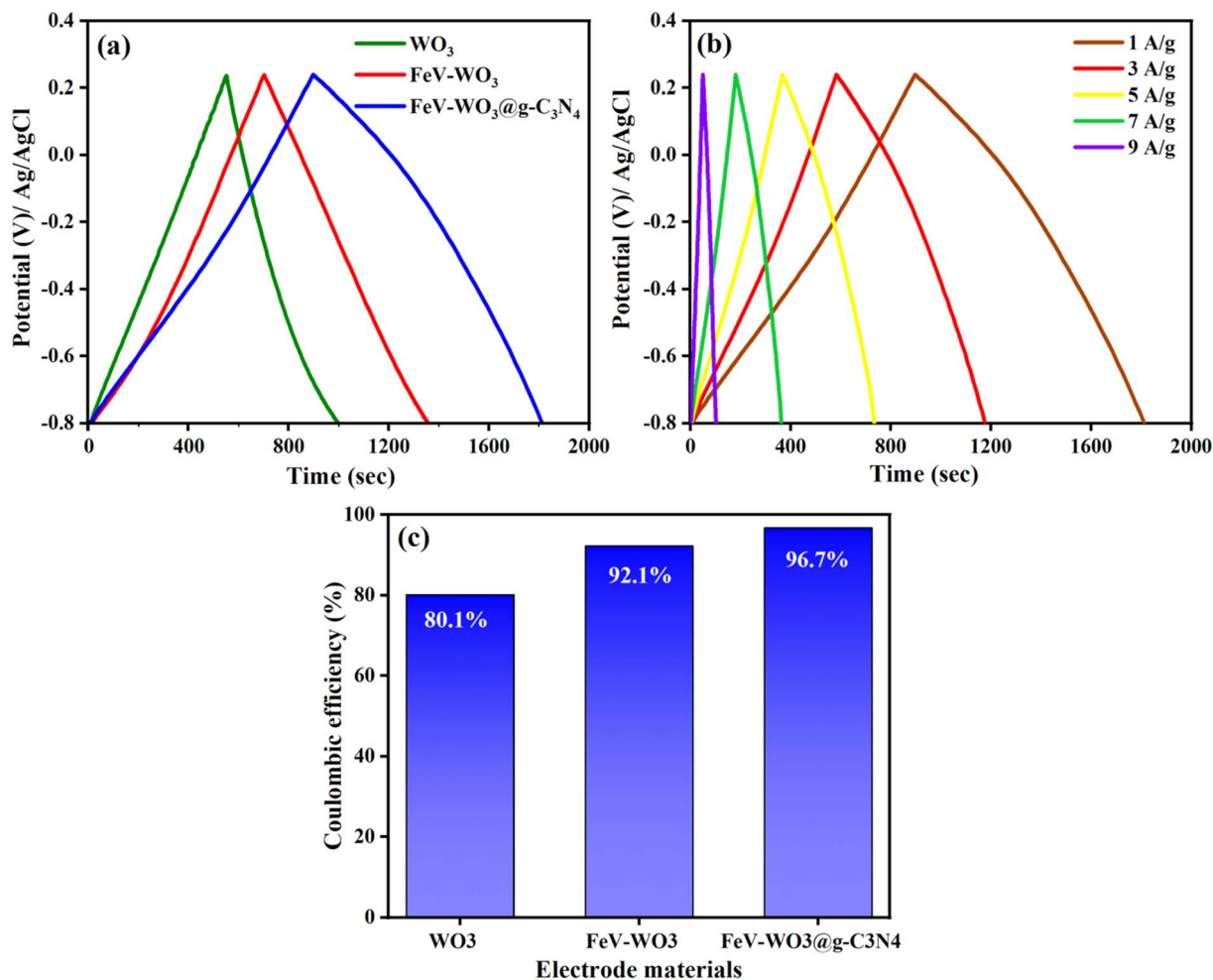


Fig. 12 (a) GCD curves of WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> at 1 A g<sup>-1</sup>, (b) GCD plots of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> at different current densities, and (c) coulombic efficiency (%) of WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>.

resistance.<sup>3</sup> Further, a comparison of different performance parameters (specific capacitance, cyclic stability, and coulombic efficiency) for FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> with already reported similar electrode materials in Table 3 shows comparable or even greater electrochemical response of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>.

EIS study is performed for the analysis of ion transfer and electrical conductivity of the prepared electrodes *i.e.*, WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>. EIS measurements of the WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> in 1 M Na<sub>2</sub>SO<sub>4</sub> were performed in the frequency range of 0.1 Hz–100 kHz, and corresponding Nyquist

plots are presented in Fig. 13(a)–(c). Nyquist plot has two separate zones, the high frequency portion usually represented by an arc, and the low frequency zone by a sloped line.<sup>92</sup> The real impedance axis in Nyquist provides internal resistance of active material and the capacitance behavior of the electrode can be easily analyzed by the imaginary component of the Nyquist plot. The internal resistance or equivalent series resistance ( $E_{SR}$ ) is represented by Nyquist's intersect with the real part of Nyquist plot.  $E_{SR}$  values of WO<sub>3</sub>, FeV-WO<sub>3</sub>, and FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> were 2.22 Ω, 1.92 Ω, and 1.82 Ω, respectively. FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> has low value of  $E_{SR}$  which

Table 3 Comparison of performance parameters of FeV-WO<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub> with already reported similar electrode materials

| Electrode  | Specific capacitance (F g <sup>-1</sup> ) | Cyclic stability (%) | Coulombic efficiency (%) | Ref.         |
|--|---|----------------------|--------------------------|--------------|
| h-WO <sub>3</sub> nanoflakes                         | 588                                       | 95.5%@5000 cycles    | 90.7%                    | 86           |
| WO <sub>3</sub> nanofibers                           | 436                                       | 98%@5000 cycles      | 98%                      | 87           |
| Nb doped WO <sub>3</sub> //MnO <sub>2</sub>          | 126                                       | 90%@2000 cycles      | 96%                      | 88           |
| WO <sub>3</sub> /graphene                            | 761                                       | 99.2%@5000 cycles    | 98.2%                    | 89           |
| WO <sub>3</sub> /carbon fiber                        | 385                                       | 88%@1000 cycles      | —                        | 90           |
| RGO-CNT-WO <sub>3</sub>                              | 691.38                                    | 89.09%@5000 cycles   | 98.4%                    | 91           |
| FeV-WO <sub>3</sub> @g-C <sub>3</sub> N <sub>4</sub> | 1033.68                                   | 97.3%@2000 cycles    | 96.7%                    | Current work |



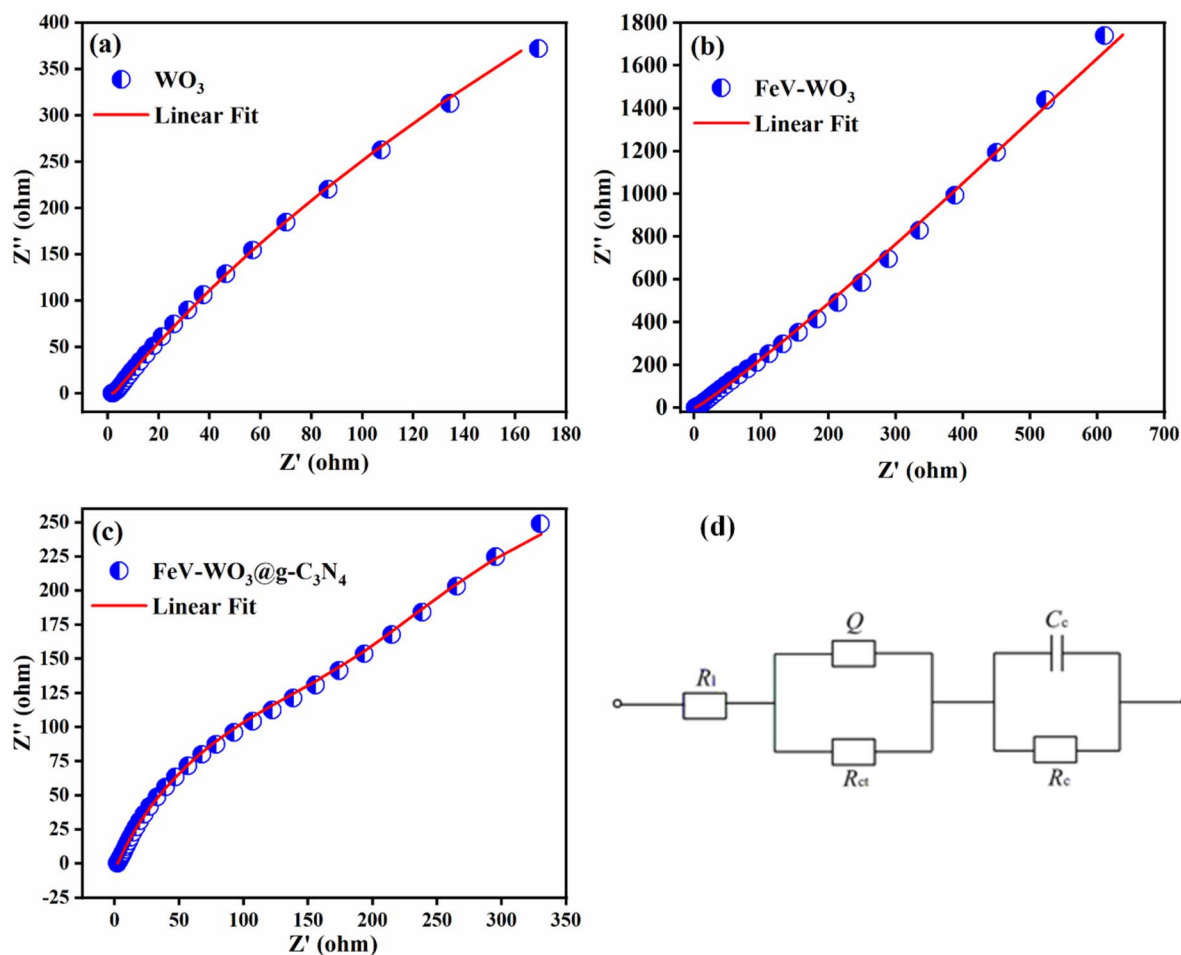


Fig. 13 Nyquist plot of (a)  $\text{WO}_3$ , (b)  $\text{FeV-WO}_3$ , (c)  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$ , and (d) equivalent circuit diagram.

shows it contains low internal resistance and efficient electrical conductance. The charge-transfer resistance ( $R_{CT}$ ) at electrode-electrolyte interface can be determined by the diameter of semicircle at high frequency region. In case of distorted semicircle,  $R_{CT}$  value can be determined by the extrapolation of arc on real axis.  $R_{CT}$  values for  $\text{WO}_3$ ,  $\text{FeV-WO}_3$ , and  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  were 1.53  $\Omega$ , 1.28  $\Omega$ , and 0.65  $\Omega$ , respectively.  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  has a smaller value of charge transfer resistance than  $\text{WO}_3$  and  $\text{FeV-WO}_3$ . The line at 45  $^\circ\text{C}$  parallel to the imaginary part at a higher frequency zone defines the diffusion or Warburg resistance ( $R_w$ ) that is primarily related to the diffusive resistance of the electrolyte ions in electrode. Electrodes showing a vertical line towards the low frequency zone of the Nyquist plot illustrate the ideal behavior of the electrode for supercapacitors.<sup>93</sup> Equivalent circuit fitted to EIS data of prepared electrodes is shown in Fig. 13(d).

## 5. Conclusions

In short, the conductive material  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  was prepared by wet chemical approach for supercapacitor study. When electrochemical studies were performed, prepared electrodes  $\text{WO}_3$ ,  $\text{FeV-WO}_3$ , and  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  revealed specific capacitance of 422.76  $\text{F g}^{-1}$ , 669.76  $\text{F g}^{-1}$ , and 1033.68  $\text{F g}^{-1}$  at scan rate 5  $\text{mV s}^{-1}$ ,

respectively in 1 M  $\text{Na}_2\text{SO}_4$  electrolyte solution.  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  exhibited a higher value of specific capacitance and also maintained its shape without any significant change in current even after 2000 cycles which confirms that it is the potential material for supercapacitor application. GCD study showed composite exhibited greater discharge time than other electrodes of about 867 s which reveals that it has greater charge storage ability. It is concluded from EIS measurements that  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  has less electrochemical impedance than  $\text{WO}_3$  and  $\text{FeV-WO}_3$ . The results demonstrated that  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  has the best structural, morphological, and componential properties for optimal efficiency. Therefore, the remarkable electrochemical behavior of  $\text{FeV-WO}_3@g\text{-C}_3\text{N}_4$  suggests that it can be employed as an effective supercapacitor electrode.

## Conflicts of interest

There are no conflicts to declare.

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