



# Article Electro-Oxidation of Metal Oxide-Fabricated Graphitic Carbon Nitride for Hydrogen Production via Water Splitting

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Abstract: Hydrogen is a great sourcez of energy due to having zero emission of carbon-based contents. It is found primarily in water, which is abundant and renewable. For electrochemical splitting of water molecules, it is necessary to use catalytic materials that minimize energy consumption. As a famous carbon material, graphitic carbon nitride, with its excellent physicochemical properties and diversified functionalities, presents great potential in electrocatalytic sensing. In the present work, graphitic carbon nitride-fabricated metal tungstate nanocomposites are synthesized by the hydrothermal method to study their applications in catalysis, electrochemical sensing, and water splitting for hydrogen production. Nanocomposites using different metals, such as cobalt, manganese, strontium, tin, and nickel, were used as a precursor are synthesized via the hydrothermal process. The synthesized materials (g-C<sub>3</sub>N<sub>4</sub>/NiWO<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>/MnWO<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>/CoWO<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>/SnWO<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>/SrWO<sub>4</sub>) were characterized using different techniques, such as FTIR and XRD. The presence of a functional groups between the metal and tungstate groups was confirmed by the FTIR spectra. All the nanocomposites show a tungstate peak at 600 cm<sup>-1</sup>, while the vibrational absorption bands for metals appear in the range of  $400-600 \text{ cm}^{-1}$ . X-ray diffraction (XRD) shows that the characteristic peaks matched with the JCPDS in the literature, which confirmed the successful formation of all nanocomposites. The electrochemical active surface area is calculated by taking cyclic voltammograms of the potassium-ferrocyanide redox couple. Among the entire series of metal tungstate, the  $g-C_3N_4$ /NiWO<sub>4</sub> has a large surface area owing to the high conductive properties towards water oxidation. In order to study the electrocatalytic activity of the as-synthesized materials, electrochemical water splitting is performed by cyclic voltammetry in alkaline medium. All the synthesized materials proved to be efficient catalysts with enhanced conductive properties towards water oxidation. Among the entire series, g-C<sub>3</sub>N<sub>4</sub>-NiWO<sub>4</sub> is a very efficient electrocatalyst owing to its higher active surface area and conductive activity. The order of electrocatalytic sensing of the different composites is:  $g-C_3N_4-NiWO_4 > g-C_3N_4-SrWO_4 > g-C_3N_4-CoWO_4 > g-C_3N_4-SnWO_4 > g-C_3N_4-MnWO_4$ . Studies on electrochemically synthesized electrocatalysts revealed their catalytic activity, indicating their potential as electrode materials for direct hydrogen evolution for power generation.

Keywords: hydrothermal; cyclic voltammetry; surface area; electrochemical; sensor



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# 1. Introduction

The rapid growth of energy use demands more sustainable and renewable energy production. The primary renewable energy resources such as solar and wind power are ecofriendly, but they possess seasonal intermittence and variabilities due to regional differences. To avoid such problems, such unstable energy sources should be replaced with the stable hydrogen energy [1]. The production of hydrogen is becoming increasingly popular due to its environment-friendly qualities and potential as a source of energy that is clean, non-polluting, and recyclable. In coping with the future energy crisis, hydrogen can play an important role [2]. In view of hydrogen generation, water electrolysis is a common and efficient method. Generally, water splitting is based on the two half processes: the cathodic oxygen evolution reaction (OER) and the anodic hydrogen evolution reaction (HER). Although water electrocatalysis produces very pure and ecofriendly hydrogen, due to the sluggish kinetics of OER and HER and large overpotential value, the practice of energy generation via water splitting is limited [3]. To solve this problem, the use of electrocatalysts should be implemented in order to minimize the overpotential value for cathodic hydrogen evolution (HER) and anodic oxygen evolution (OER) [4]. The electrocatalysts make the water splitting an energy-efficient process [5]. Recently, research on electrochemical water splitting using various electrocatalysts has been conducted to achieve this objective [4]. The noble metals such as platinum-, iridium-, and ruthenium-based nanomaterials proved to be efficient regarding HER and ORE processes [6,7]. The existence of such catalysts makes them indispensable for many technologically significant chemical processes, although their spontaneous aggregation and growth limit the lifetime and efficiency. Additionally, the ultrahigh price of noble metals has severely limited their future use. Due to the rapid development of modern industry, a critical need of today is highly active, stable, low-cost, and recyclable nanomaterial alternatives to these noble metals, designed for water splitting [8]. Recently, the conductive polymers (CPs) have been shown as a potential alternative to Pt-based materials due to their high electrical properties, large surface area, and greater physical and chemical stability [9-11]. Among the 2D CPs, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is a graphene-like material having excellent structural features, such as high porosity, large surface area, and greater content of nitrogen.  $g-C_3N_4$  has wide applications in electrochemical sensing, optoelectronics, electrochemical oxidations, and energy storage and conversion devices [12,13]. g-C<sub>3</sub>N<sub>4</sub> can be used as a good supportive material for manufacturing 3D nanomaterials for different electrochemical applications. Doping of different nanomaterials with  $g-C_3N_4$  generates highly active electrode materials by connection within hybrids [14]. In the past few years, scientists have enhanced the properties of CPs by doping with transition metals/metal oxides [15]. Recently, a series of low-cost metal tungstates, such as  $Bi_2WO_6$ , CuWO<sub>4</sub>, NiWO<sub>4</sub>, and CoWO<sub>4</sub>, have been extensively studied as efficient dopants, with g-C<sub>3</sub>N<sub>4</sub> showing various applications because of its outstanding optical, magnetic, and catalytic properties [16]. Hence, from these studies, it seems that by doping  $g-C_3N_4$  with CoWO<sub>4</sub> [17] and NiWO<sub>4</sub> [18], its photocatalytic activity is enhanced. Similarly, strontium, tin, manganese, zirconium, and cobalt are the most promising transition metals and are reported as dopants with  $g-C_3N_4$  for numerous applications [15,19,20]. These metals have a large bandgap, rendering them with weak ion transport kinetics as semiconductors or even insulators [19], and electrode film pulverization as a result of the pronounced expansion and contraction of volume during the charging/discharging processes [20].

Motivated by these results, we have designed this research work to explore the catalytic activity of transition metal tungstate-fabricated graphitic carbon nitride for electrochemical applications. In this work, the nanocomposites ( $g-C_3N_4-NiWO_4$ ,  $g-C_3N_4-MnWO_4$ ,  $g-C_3N_4$ -SnWO<sub>4</sub>,  $g-C_3N_4-CoWO_4$ ,  $g-C_3N_4-SrWO_4$ ) were synthesized via the hydrothermal method and characterized by XRD, FTIR, and electrochemical cyclic voltammetry. The study of the electrocatalytic splitting of water for hydrogen production was carried out in alkaline medium via cyclic voltammetry. All the synthesized nanocomposites represent excellent catalytic activity towards water oxidation.

## 2. Materials and Methods

## 2.1. Materials

Melamine (purity: 99.95%), cyanuric acid (purity: >99%), sodium tungstate (Sigma Aldrich, St. Louis, MO, USA), sodium hydroxide (Sigma Aldrich), potassium hexacyanoferrate (III) ( $K_4$ [Fe(CN)<sub>6</sub>]), alumina powder, nafion, and different metal precursors were used. All chemicals were purchased from Sigma Aldrich (St. Louis, MO, USA).

# 2.2. Preparation of g-C<sub>3</sub>N<sub>4</sub>

Following the protocol of Vilian et al.,  $C_3N_4$  was prepared [21]. The melamine and cyanuric acid were dissolved in water (75 mL) and ultrasonically maintained for 4 h. An oven (Memmert, Germany) was used at 200 °C for 12 h to heat the solution after sonication in a 100 mL stainless Teflon lining. Centrifugation, followed by cleaning with ethanol and water, was performed to eradicate any remaining contaminations from the precipitate, then centrifuging was carried out at 5000 RPM for 30 min (Figure 1). After drying at 100 °C for 24 h, the precipitate was removed. Consequently, g-C<sub>3</sub>N<sub>4</sub> (Vilian et al., 2020) was synthesized [21].



Figure 1. Schematic representation of the formation of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>).

#### 2.3. Preparation of g-C<sub>3</sub>N<sub>4</sub>/Metal Tungstate Composite

The graphitic carbon nitride  $g-C_3N_4$ /MetalWO<sub>4</sub> nanocomposite was synthesized by utilizing a simple hydrothermal procedure without any surfactants. Initially, a solution of sodium tungstate and graphitic carbon nitride was made. For this purpose, 0.01 g of g-C<sub>3</sub>N<sub>4</sub> and 15 mM of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O were placed in 37 mL of deionized water. This solution was then kept under sonication for 20 min. The temperature was set at room temperature. After sonication, the mixture was placed aside. Then, 15 mM of salt solution in deionized water was prepared and added into the above mixture to form a homogeneous solution, and 1 mL of aqueous NaOH solution (0.1 M) was gradually added to the homogeneous solution. The mixture solution was then dispensed into an autoclave and heated at 180 °C for 12 h. After autoclaving, the resulting mixture was centrifuged to obtain the maximum analyte. To extract the excess unreacted starting materials, the obtained precipitate was collected and thoroughly rinsed three times with ethanol and water and desiccated at 60 °C. Finally, the resulting precipitation was strengthened in a vacuum oven at 300 °C for five hours to attain the g- $C_3N_4$ /MetalWO<sub>4</sub> nanocomposites. The obtained g- $C_3N_4$ /MetalWO<sub>4</sub> nanocomposite was circulated in ethanol to perform electrochemical measurements in Figure 2.



Figure 2. Schematic synthesis of graphitic carbon nitride-fabricated metal tungstate nanocomposite.

#### 2.4. Electrochemical Studies

The electrochemical water oxidation of all synthesized nanocomposites was studied by using the Gamry Potentiostat interface 1000 (Gamry, Warminster, PA, USA) with a 3-electrode cell (100 mL) assembly in alkaline medium. The working electrode was glassy carbon (GC), the counter electrode was platinum wire (Pt), and the reference electrode was silver/silver chloride (Ag/AgCl). Before modification, the surface of glassy carbon was cleaned with alumina slurry by polishing the electrode in a figure eight motion for 5 min. Then, it was rinsed with deionized water and sonicated for 1 min in deionized water to remove remnants of alumina powder. It was dried at room temperature. The catalyst was then deposited on the GC surface by the drop casting method, where 5% nafion was used as a binder.

## 3. Characterization Studies

## 3.1. Fourier-Transform Infrared (FTIR) Spectroscopy

The chemical and structural characteristics of nanocomposites, as well as their atomic and molecular vibrations, were investigated using FTIR (Nicolet 5PC, Nicolet Analytical Instrument (Protea, Cambridgeshire, UK) in a 500 to 4000 cm<sup>-1</sup> range. The FTIR spectrum of the cobalt tungstate-fabricated nanocomposite is depicted in Figure 3, where the two prominent peaks appeared at 1627.5 and 3350 cm<sup>-1</sup>, representing N-H bond and hydroxyl bond stretching vibration, respectively [22]. The conjugated g-C<sub>3</sub>N<sub>4</sub>-based heterocycles are represented by several absorption peaks in the 1600–1200 cm<sup>-1</sup> region [21], which appeared in nearly all spectra of g-C<sub>3</sub>N<sub>4</sub>/MetalWO<sub>4</sub>. The band at 611.8 cm<sup>-1</sup> corresponds to Co-O-W symmetric vibration [23].

Figure 4 presents the FTIR spectrum of  $g-C_3N_4/MnWO_4$ . There should be obvious peaks at 875, 827, 710, 605, and 512 cm<sup>-1</sup> for pristine MnWO<sub>4</sub>. The peaks at 870, 704, 621, and 514 cm<sup>-1</sup> correspond to the W–O (symmetric), W–O (asymmetric), Mn–O, and Mn–O–Mn stretching vibrations, respectively, which confirms the formation of manganese tungstate [21]. In Figure 4, two strong peaks appeared at 794 and 670 cm<sup>-1</sup>, demonstrating W–O (symmetric) and Mn–O–Mn stretching vibrations, respectively. Hence, Figure 4 confirms the successful preparation of  $g-C_3N_4/MnWO_4$ .

The FTIR spectrum of graphitic carbon nitride fabricated on nickel tungstate is shown in Figure 5. Strong peaks appeared at 1621 and 3322 cm<sup>-1</sup>, showing conjugation between graphitic carbon nitride and metal oxide, as in previous spectra. Peaks in the series below  $500 \text{ cm}^{-1}$  are due to the vibrations of the NiO<sub>6</sub> polyhedron [24], which is not observed in this figure as the spectrum range is from 500 to 1500 cm<sup>-1</sup>.



**Figure 3.** FTIR spectrum of g-C<sub>3</sub>N<sub>4</sub>-CoWO<sub>4</sub>.



**Figure 4.** FTIR spectrum of  $g-C_3N_4$ -MnWO<sub>4</sub>.



Figure 5. FTIR spectrum of g-C<sub>3</sub>N<sub>4</sub>-NiWO<sub>4</sub>.

The FTIR of the tin tungstate–graphitic carbon nitride sample in Figure 6 depicts a band at  $1000 \text{ cm}^{-1}$  which is due to the W=O bond. The band at  $650 \text{ cm}^{-1}$  corresponds to Sn-O vibrational modes, which slightly appeared in Figure 6.



Figure 6. FTIR spectrum of g-C<sub>3</sub>N<sub>4</sub>-SnWO<sub>4</sub>.

In Figure 7, the strong peak at 768 cm<sup>-1</sup> is due to the W-O bond in the tetrahedral. The peak at 3350 cm<sup>-1</sup> is due to OH stretching vibrations. Absorption peaks at 471 cm<sup>-1</sup> are due to the bond between strontium and oxygen [25], which did not appear here due to the selected frequency range, which is 500–1500 cm<sup>-1</sup>.



**Figure 7.** FTIR spectrum of C<sub>3</sub>N<sub>4</sub>-SrWO<sub>4</sub>.

#### 3.2. X-ray Diffraction (XRD)

X-ray diffraction (PANalytical X'PERT High Score's diffractometer, Malvern, UK) patterns of nanocomposites prepared by the hydrothermal method are shown in Figure 8. All the diffraction peaks in Figure 8 are sharp, indicating the good crystallinity of the material. Figure 8a represents the peaks of 2 $\theta$  for g-C<sub>3</sub>N<sub>4</sub>/SnWO<sub>4</sub> at 28.3° and 53.1° with crystallographic plans of (121) and (161), with JCPDS card No. 29-1354 [26], which confirms the formation of orthorhombic  $\alpha$ -SnWO<sub>4</sub>. The spectrum in Figure 8b shows the XRD of g-C<sub>3</sub>N<sub>4</sub>/MnWO<sub>4</sub>, which shows intensity peaks for MnWO<sub>4</sub> at 30.1°, 30.57°, 36.25°, and

 $67.1^{\circ}$ , with crystal lattice (-111), (111), (120), and (140), respectively, with JCPDS card No. 72-0478 [27], along with the low-intensity peak of  $g-C_3N_4$  at 26.7° (002). This spectrum in Figure 8b depicts the formation of g-C<sub>3</sub>N<sub>4</sub>/MnWO<sub>4</sub>. The XRD spectrum in Figure 8c of  $g-C_3N_4/CoWO_4$  shows the characteristic peak of  $g-C_3N_4$  at 13.1°, indexed as (100) with JCPDS card No. 50-1512 [28], and this is due to the in-plane structural packing motif. The peaks for CoWO<sub>4</sub> appeared at  $30.8^\circ$ ,  $36.4^\circ$ , and  $54.3^\circ$ , indexed as (111), (200), and (202), respectively, with JCPDS card No. 72-0479 [29]. The peaks of g-C<sub>3</sub>N<sub>4</sub>/SrWO<sub>4</sub> presented in Figure 8d are 33.6° and 55.8°, with corresponding miller indices (204) and (312) and JCPDS card No. 08-0490, which agree well with the reported data of SrWO<sub>4</sub> for Scheelite phase [30]. Figure 8e represents the XRD spectrum of  $g-C_3N_4/NiWO_4$ , having peaks at  $31.1^\circ$ ,  $36.2^\circ$ , 55.4°, and 65.2° for NiWO<sub>4</sub> with JCPDS card No. 15-0755 [31]; thus, this confirmed the synthesis of  $g-C_3N_4/NiWO_4$ . The intensity of the peaks in many spectra decreased and the peak width increased, which indicated the interaction between metal tungstate and  $C_3N_4$  nanoparticles, and thus confirmed the successful formation of nanocomposites. No characteristic peaks for other impurity phases were observed in all five XRD patterns, showing that the selected synthetic method is a feasible route to prepare pure phases of catalysts.



Figure 8. XRD patterns of (a)  $g-C_3N_4$ , (b)  $g-C_3N_4/MnWO_4$ , (c)  $g-C_3N_4/CoWO_4$ , (d)  $g-C_3N_4/SrWO_4$  and (e)  $g-C_3N_4/NiWO_4$  nanocomposites.

The size of the prepared materials was calculated by using the Debye–Scherrer equation [32]:

$$D_{avrg} = \frac{\kappa \lambda}{\beta \, \cos \theta} \tag{1}$$

where  $D_{avrg}$  is equal to the average crystallite size,  $\lambda$  is the X-ray wavelength,  $\theta$  is the Bragg angle of the desired peak, and  $\beta$  is the line broadening evaluated from the peak width at half height. The average crystalline size of all synthesized particles is presented in Table 1. In XRD patterns, the peak width is inversely proportional to the crystallite size. Normally, nanoparticles of small-sized peaks have a small particle size, while those of sharp peaks have large particle sizes. The small particle size is responsible for more catalytic activity [33].

Samples	D <sub>avrg</sub> (XRD) (nm)		
g-C <sub>3</sub> N <sub>4</sub> /SnWO <sub>4</sub>	9.0		
g-C <sub>3</sub> N <sub>4</sub> /MnWO <sub>4</sub>	16.3		
g-C <sub>3</sub> N <sub>4</sub> /CoWO <sub>4</sub>	52.6		
g-C <sub>3</sub> N <sub>4</sub> /SrWO <sub>4</sub>	84.4		
g-C <sub>3</sub> N <sub>4</sub> /NiWO <sub>4</sub>	30.3		

Table 1. Calculated values of Davrg.

#### 3.3. Estimation of Active Surface Area of Modified Electrode

To determine the active surface area of electrodes, which is altered by catalysts having diverse loadings of nanocomposites, cyclic voltammograms were recorded at a scan rate of 100 mV s<sup>-1</sup> in a 0.1 M KCl solution, with 5 mM of potassium ferrocyanide as a model redox mediator (Figure 9). The peak currents show that the highest value corresponds to the NiWO<sub>4</sub>-modified electrode. This means that the sample NiWO<sub>4</sub>-presents better conductive properties towards the redox probe as related to the rest of the catalysts.



**Figure 9.** Cyclic voltammogram in 5 mM of potassium Ferrocyanide redox couple, with 0.1 M KCl as the supporting electrolyte at a 100 mV s<sup>-1</sup> sweep rate at the surface of the modified GC.

The active surface area was estimated using the Randles–Sevcik equation for reversible reactions [34]:

$$Ip_a = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} C$$
(2)

where D is the diffusion coefficient ( $0.76 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ ), n = 1, and C is the concentration of analytes (5 mM).

From Table 2, it can be seen that  $g-C_3N_4$  with nickel tungstate presented a higher surface area as compared to the other metal tungstates. This means that the nickel tungstate-fabricated graphitic carbon nitride is an efficient electrocatalyst towards an electrochemical redox reaction.

Samples	Active Surface Area (cm <sup>-2</sup> )		
g-C <sub>3</sub> N <sub>4</sub> /SnWO <sub>4</sub>	0.061		
g-C <sub>3</sub> N <sub>4</sub> /MnWO <sub>4</sub>	0.050		
g-C <sub>3</sub> N <sub>4</sub> /CoWO <sub>4</sub>	0.068		
g-C <sub>3</sub> N <sub>4</sub> /SrWO <sub>4</sub>	0.081		
g-C <sub>3</sub> N <sub>4</sub> /NiWO <sub>4</sub>	0.088		

Table 2. Active surface area calculated for modified electrodes.

## 4. Electrochemical Water Oxidation

CV (Gamry Interface 1000) was used to perform electrochemical studies, such as water oxidation. Three electrodes were utilized for the experiment: modified GC as a working electrode, *Pt-wire* as a counter electrode, and silver-silver chloride as a reference electrode. Water oxidation was carried out in a 1 M KOH solution in a potential window ranging from 0.5 to 1.8 V at different scan rates (10 to 100 mV s<sup>-1</sup>). The cyclic voltammetry behaviors of nanocomposites were used to investigate the redox kinetics of the electrodes (Figure 10a-e). The anodic peak current with a growing scan rate from 10 to  $100 \text{ mV s}^{-1}$  was represented, which shows that the current increased with the increasing sweep rate, from 1.25 to 4.46 mA for g- $C_3N_4$ -CoWO<sub>4</sub>/GC, from 0.17 to 0.45 mA for g-C<sub>3</sub>N<sub>4</sub>/MnWO<sub>4</sub>/GC, from 0.2 to 1.7 mA for g-C<sub>3</sub>N<sub>4</sub>-SnWO<sub>4</sub>/GC, from 2.5 to 6.5 mA for g- $C_3N_4$ -NiWO<sub>4</sub>/GC, and from 2.0 to 5.5 mA for g- $C_3N_4$ -SrWO<sub>4</sub>/GC, and the peak potential shifted towards higher (anodic) potentials. The onset potential for all five nanocomposites is presented in Table 3. The reported onset potential for water oxidation on  $CoWO_4$  was ~1.54 V (NHE) [35], while CoWO<sub>4</sub>-fabricated  $g-C_3N_4$  was 1.12 V (NHE). An ideal potential value for the water oxidation reaction is 1.23 V (NHE) [36–38]. From Table 3, it can be seen that all synthesized electrocatalysts presented lower onset potential values (NHE) for OER, which revealed that all the nanocomposites performed well in cyclic voltammetry, inherently possessing superior oxygen evolution activity. The peak current of different synthesized nanocomposites is shown in Figure 10f and Table 3, which was in the order:  $g-C_3N_4/NiWO_4 > g-C_3N_4/SrWO_4 > g-C_3N_4/CoWO_4 > g-C_3N_4/SnWO_4 > g-C_3N_4/MnWO_4$ . Hence, these synthesized nanocomposites are favorable for being excellent electrochemical catalysts towards water oxidation.

Samples	E <sub>onset</sub> (V)	Ip <sub>a</sub> (mA)	α	$D^{0}/10^{-6} cm^{2} s^{-1}$
g-C <sub>3</sub> N <sub>4</sub> /SnWO <sub>4</sub>	1.08 (NHE =1.23)	1.5	0.2	40.72
$g-C_3N_4/MnWO_4$	0.999 (NHE = 1.19)	0.45	0.3	14.09
g-C <sub>3</sub> N <sub>4</sub> /CoWO <sub>4</sub>	0.92 (NHE = 1.12)	4.5	0.2	130.00
$g-C_3N_4/SrWO_4$	0.86 (NHE = 1.06)	5.3	0.2	132.06
g-C <sub>3</sub> N <sub>4</sub> /NiWO <sub>4</sub>	0.80 (NHE = 1.01)	6.5	0.1	133.3

**Table 3.** Kinetics parameters for water oxidation at  $g-C_3N_4$ /MetalWO<sub>4</sub>/GC.

The linear relationship between peak current (Ip<sub>a</sub>) and scan rates ( $v^{1/2}$ ) is presented in Figure 11 and illustrates that the water oxidation on the surface of metal oxide catalysts is diffusion-controlled.

# Determination of Diffusion Coefficient (D<sup>o</sup>)

The diffusion coefficient was determined by using the Randles–Sevcik formula for irreversible reactions [32]:

$$Ip_a = 2.69 \times 10^5 \text{ n}^{3/2} \text{ AC} \times (1 - a) \text{ n} \text{ D}^{1/2} \text{ v}^{1/2}$$
(3)

where A is the surface area of the electrode (0.07 cm<sup>2</sup>), C is the concentration of KOH (1 M), N is the number of electrons for OER (2), and  $\alpha$  is the transfer coefficient (0.2–0.7). From the slope of the plot of Ip<sub>a</sub> vs.  $\nu^{1/2}$ , we obtained the diffusion coefficients tabulated in Table 3. Table 3 depicts that g-C<sub>3</sub>N<sub>4</sub>/NiWO<sub>4</sub> has a higher value of the diffusion coefficient as compared to the other catalysts, showing that g-C<sub>3</sub>N<sub>4</sub>/NiWO<sub>4</sub> nanoparticles are an excellent candidate for rapid redox reactions towards water oxidation.



**Figure 10.** CV curves of water oxidation in 1 M KOH at different sweep rates  $(10-100 \text{ mV s}^{-1})$  of: (a) g-C<sub>3</sub>N<sub>4</sub>-SnWO<sub>4</sub>, (b) g-C<sub>3</sub>N<sub>4</sub>-MnWO<sub>4</sub>, (c) gC<sub>3</sub>N<sub>4</sub>-CoWO<sub>4</sub>, (d) g-C<sub>3</sub>N<sub>4</sub>-SrWO<sub>4</sub>, and (e) g-C<sub>3</sub>N<sub>4</sub>-NiWO<sub>4</sub>. (f) Comparative peak current of all nanocomposites at 100 mV s<sup>-1</sup> in 0.1 M KOH.



**Figure 11.** Dependence of Ip<sub>a</sub> on  $v^{1/2}$  showing linear fitting for scan rates for g-C<sub>3</sub>N<sub>4</sub>/MetalWO<sub>4</sub>.

#### 5. Conclusions

The present study presented a simple fabrication strategy for the fabrication of  $g-C_3N_4$ on metal tungstates as a potential electrode material for the electrochemical splitting of water samples. Metal tungstates (nickel tungstate, copper tungstate, stannous tungstate, strontium tungstate, and manganese tungstate) were distributed on the graphitic carbon nitride surface. The composites were successfully formed, as revealed by XRD and FTIR analysis. In FTIR spectroscopy for functional group detection, all the composites showed a tungstate peak at 600 cm $^{-1}$ . X-ray diffraction (XRD) was performed at 2 theta, showing characteristic peaks according to their JCPDS card numbers. The electrochemical properties of the electrodes were confirmed via cyclic voltammetry. The g-C<sub>3</sub>N<sub>4</sub>-NiWO<sub>4</sub> composite electrode displayed a unique electrochemical sensing behavior compared to the other composite electrodes, exhibiting a high peak current and low peak potential. The order of electrocatalytic sensing of different composites towards water oxidation was: g-C<sub>3</sub>N<sub>4</sub>- $NiWO_4 > g-C_3N_4 SrWO_4 > g-C_3N_4-CoWO_4 > g-C_3N_4-SnWO_4 > g-C_3N_4-MnWO_4$ . Based on the results from the fabricated electrochemical sensor, the g-C<sub>3</sub>N<sub>4</sub>/NiWO<sub>4</sub> composite displayed the highest active surface area at  $0.088 \text{ cm}^{-2}$ . In this case, the peak current was higher and the sensitivity was also high. Aside from this,  $g-C_3N_4/NiWO_4$  can also be employed in the manufacture of electrodes used in clinical, pharmaceutical, and medical applications. As a result, the proposed modified electrode can be employed in the long term for electrocatalytic sensing, with good selectivity and reproducibility. The findings indicated that the investigated approach could be useful in regular analytical applications.

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