Bifunctional copper-zinc bimetallic tungstate nanoparticles decorated reduced graphene oxide (CuZnWO$_4$/rGO) for high-performance photocatalytic and supercapacitor application

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Abstract

In the present work, an attempt to synthesis of bimetallic copper zinc tungstate (CuZnWO$_4$) nanoparticles with reduced graphene oxide (CuZnWO$_4$/rGO) via one-step hydrothermal technique. The synthesized CuZnWO$_4$/rGO composite are characterized by Fourier transform infrared spectroscopy (FTIR), Powder X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Vis diffuse reflectance spectroscopy (UV-DRS) and Photoluminescence (PL). The photocatalytic performance is examined by the degradation of methylene blue (MB) dye under visible-light irradiation. The MB dye is almost 73 % degraded within 80 minutes. Further, the electrochemical performance of hybrid CuZnWO$_4$–rGO composite showed the specific capacity (SC) of 480 Fg$^{-1}$ at 4 Ag$^{-1}$ in 6 M KOH electrolyte with excellent cyclability conserving a capacitance retention of 127% after 5000 cycles due to increase diffusion of electrolyte ions to the electrode materials. These results support that the hybrid CuZnWO$_4$–rGO composite as an appropriate electrode material for high-performance SCs electrode and an auspicious catalyst for the degradation of dye (organic) contaminants in aqueous media.

Keywords: Bimetallic tungstate; Reduced graphene oxide; Photocatalysis; Supercapacitor
1. Introduction

In the 21st century, the manhood met massive challenges in energy crisis and ecological pollution. Owing to the increasing human population and industrialization, fossil fuels and coal are highly utilized and depleted very soon. The environmental problems accompanying with direct release of harmful organic pollutants from the textile industry to water sources are a serious issue[1–3]. Therefore, the investigation of fast and effective ecological protection and energy storage technologies has become a hottest theme for researchers. Generally various kinds of materials are used as a catalyst for photocatalytic activity and electrodes for energy storage device (such as metal oxides, conducting polymers, carbonaceous materials, metal sulfides and etc.,) [4–7]. Regrettably, most of the catalysts and electrodes suffer from low-light energy garnering and quick extermination of electron-hole pairs. Among these materials, the metal tungstate’s has a significant consideration owing to their immeasurably wide-range of applications in various fields such as supercapacitors (SCs), photocatalysis, optical devices, structural, electrical/electronics, humidity sensors, metal-ion batteries and electrocatalysis[8,9].

Chemical contaminants such as dyes emitted from the clothing, food, and leather industries pose a major environmental threat. Photocatalytic nanomaterials are the most effective agents for the degradation of toxic organic dyes, such as methylene blue (MB), rhodamine-B (RhB) and methyl orange (MO). Due to the extreme huge release from different factories, it causes significant adverse effects on the environment and critically increases water contamination, thus effectively disrupts the ecosystem[10]. Zinc tungstate (ZnWO₄), a typical traditional catalyst, has been extensively used as photo-catalyst and applied in photocatalytic degradation of dyes (organic contaminants) due to its extraordinary aspects of cost effectiveness, high stability, non-toxicity, high quantum yield, commercial accessibility and outstanding photoelectrical performance. However, the pure ZnWO₄ shows feeblish visible-light photocatalytic activity due to the wide range of band gap.

Electrochemical capacitors or supercapacitors (SCs) are a new class of electric energy storage devices, they get more consideration due to its extraordinary properties such as high cyclability, high power/energy density, and they could rapidly deliver greater energy-density than conversional capacitors and simultaneously larger power density than secondary batteries[13]. The performance of SCs is based on the electrodes, so it plays a major role in SCs. Nowadays various kinds of materials are used as a SCs electrode they are carbonaceous materials
(such as: activate carbon, graphene, carbon quantum dots, carbon nano tubes and etc.) metal oxides (MOs) (such as: NiO, V2O5, Fe2O3, CuO and etc.) and conducting polymers (CPs) (such as: polyaniline, polypyrrole, polyindole, polythiophene and etc.) [14]. The major disadvantage of the SCs is low energy density, where does not meet the future demand of portable electrical/electronic devices and modern electric vehicles [15]. Similarly, the commercializing of SCs is still stuck by the moderately poor-overall performance, like the carbonaceous materials show low specific capacitance (Cs), low conductivity of MOs as well as poor cyclability of conducting polymers (CPs). The current research is fully focused on the synthesis of novel/hybrid nano-structured electrode materials to enhance the energy density of SCs. Among the various electrode materials, the metal tungstate’s (MWO4; M = Ni, Cu, Pb, Mn, Co, Zn and etc.) are recognized as effective resources consuming adaptable chemical properties. The MWO4 attract more attention in past few decays owing to its astonishing physio-chemical assets which makes them it as a potential and auspicious materials for various applications in the arena of photocatalytic activity, energy storage, electrical/electronics, antimicrobial, magnetic, electrocatalysis, and ceramics [16,17].

In this present work, a copper zinc bimetallic tungstate (CuZnWO4) nanoparticle decorated reduced graphene oxide (rGO) (CuZnWO4/rGO) nanocomposites synthesized via hydrothermal technique. As synthesized materials are used as an electrode for SCs and catalyst for photocatalytic applications. CuZnWO4 and CuZnWO4-rGO are examined by XRD, FTIR, SEM, and optical study of UV-DRS and photoluminescence. Electrochemical behavior is investigated by cyclic voltammetry (CV), galvanic charge discharge (GCD) and impedance (EIS) in 6 M KOH aqueous electrolyte and the photocatalytic activity are evaluated by methylene blue degradation. The above results are projected that the CuZnWO4/rGO nanocomposite assist as an effective electrode SCs electrode material for and photocatalytic applications.

2. Experimental

2.1. Chemicals and materials

Copper acetate (Sigma-Aldrich), zinc acetate (Merck), sodium tungstate (SD Fine), Cetyltrimethylammonium bromide (Sigma-Aldrich). All of the above-mentioned chemicals
purchased were analytical grade and used without any further purification. The whole reaction was carried out using water and ethanol as solvents.

2.2 Synthesis of CuZnWO$_4$ and CuZnWO$_4$-rGO Composite

Reduced graphene oxide was synthesized by hummers method and followed by reduction using ammonia in hydrothermal method [18]. CuZnWO$_4$ bimetallic tungstate was synthesized by hydrothermal method using copper acetate and zinc acetate as a precursor. The precursors of copper and zinc (1:1 ratio, 0.2 M each) and 4 M CTAB was dissolved in 15 mL distilled under continues stirring for 30 minutes. Further, as prepared 0.4 M Na$_2$WO$_4$·2H$_2$O was added drop by drop into the above solution under continuous stirring, a thick light green coloration was developed. Then the resultant solution was transferred into a 50 mL of Teflon-lined stainless-steel autoclave and heated for 180 °C for overnight in hot air oven. The attained product was washed several times and followed by centrifuge, the obtained precipitate was dried overnight in a hot air oven at 60 °C and annealed for 450 °C at 2 h.

A composite of CuZnWO$_4$/rGO hybrid nanostructures was prepared using the same procedure with addition of reduced graphene oxide (rGO). Fig.1 showed the schematic illustration of CuZnWO$_4$ and CuZnWO$_4$/rGO composite.

2.3. Characterization

The crystal nature of the synthesized samples was examined by Powder X-ray diffraction (XRD) from the range of $2\theta$ ~ 10 – 80, Ni filtered Cu Ka radiation as a source. Fourier transform inferred spectra (FTIR) were investigated using Perkin-Elmer instrument (USA) in the range of 400-400 cm$^{-1}$ with KBR as a reference material at room temperature. The surface morphology of CuZnWO$_4$ and CuZnWO$_4$-rGO composite were visualized by scanning electron microscope (SEM, Hitachi SU-70, Japan) running at 25 kV an accelerating voltage. UV–visible diffuse reflectance spectra (UV-DRS) were recorded by Lambda-900 spectrometer in the range of 200-800 nm.

2.4. Photocatalytic activity

The photocatalytic performance of the synthesized materials was examined against the photo-degradation of synthetic dye methylene blue (MB) under visible light at ambient temperature. Initially 100 mg of methylene blue (MB) was added into 100 mL of de-ionized water and stirred well for 30 minutes. 1 mL of this aqueous solution was introduced into reactor
with 50 mg of synthesized materials at constant stirring. After that, 5 mL of the solution was collected with the time interval of 10 minutes up to 80 minutes. The degradation efficiency of the synthesized samples was calculated by the following equation[19].

\[ D\% = \frac{c_0 - c_t}{c_0} \times 100 \] (1)

Where, \( c_0 \) is the major absorption intensity of MB dye at 0 min and \( c_t \) is the dye degradation peak intensity under visible-light for the time \( t \) (10, 20, 30, 40, 50, 60, 70, and 80 min).

2.5. Electrochemical performance

The electrochemical performance of the synthesized electrode material was examined using a three-electrode cell in 3 M KOH aqueous electrolyte solution within the potential-window of 0 - 0.6 V on a biologic S-50 electrochemical workstation. Cyclic voltammogram (CV) and galvanostatic charge and discharge (GCD) and electrochemical impedance spectra (EIS) were performed. CV was used to know the potential of the electrodes and GCD was used to examine the specific capacitance of the electrode and EIS was used to analyze the resistance of the electrode material.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 2(a-b) illustrates the XRD spectrum of CuZnWO₄ and CuZnWO₄-rGO composite. Fig. 2(a) shows the XRD pattern of CuZnWO₄, where indexed 2θ value of 15.47 °, 18.85 °, 23.82 °, 24.59 °, 25.84 °, 28.98 °, 30.45 °, 36.5 °, 38.5 °, 41.2 °, 44.9 °, 48.56 °, 51.6 °, 53.5 °, 61.8 °, 62.6 °, 65.03 ° and 68.07 ° corresponding to (010), (100), (011), (110), (101), (111), (111), (021), (200), (102), (112), (112), (130), (202), (113), (230), (040) and (041) diffraction planes, respectively. However, some of the planes are comparative to both metals Cu and Zn in bimetallic tungstate. The XRD diffraction pattern of CuZnWO₄ accord with the pristine structural phase of CuWO₄ and ZnWO₄ in standard JCPDS card no. 80-1918and89-7624 respectively[20,21]. The CuZnWO₄-rGO nanocomposite XRD pattern is shown in Fig.2(b), where illustrates the similar peaks as like Fig. 2a corresponds to CuZnWO₄ but no other characteristic peaks for rGO is not clearly visible in CuZnWO₄-rGO XRD pattern, due to the shielding effect by strong diffraction peaks of CuZnWO₄ particles but rGO peaks are merged with CuZnWO₄ peaks inCuZnWO₄-rGO composite [22,23].
3.2. Fourier transform inferred spectra analysis (FT-IR)

FT-IR spectra are used to investigate the surface state and functional groups of the prepared samples. Fig. 3 shows, FTIR spectra of the CuZnWO₄ and CuZnWO₄/rGO nanocomposite. Fig. 3(a) display the FTIR spectrum of CuZnWO₄, the peak at 3000-3400 cm⁻¹ corresponds to the hydroxyl group (OH)[24], the absorption peaks at 460 cm⁻¹, 595 cm⁻¹ and 625 cm⁻¹ are associated with the stretching and bending vibration of M-O (M=Cu and Zn). While the band at 806 cm⁻¹ is related to the bending/stretching vibration of W-O cm⁻¹ for tetrahedral WO₄[25,26] and the peak at 890 cm⁻¹ is associated with the stretching/bending vibration of M-W-O groups[27]. Fig. 3(b) shows the FTIR spectrum of CuZnWO₄/rGO composite. The peaks which were obtained in CuZnWO₄ spectra are also present in CuZnWO₄/rGO composite and some other absorption bands are obtained with respect to rGO [27]. The peak at 1716 cm⁻¹ is allocated for the C=C skeleton of rGO[28]. Therefore, the results shown in Fig. 3. is an evidence to confirm a synthesized product as CuZnWO₄/rGO nanocomposite.

3.3. UV-Vis DRS and Photoluminescence analysis

The light absorption property of the synthesized samples is analyzed using UV-Vis diffuse reflection spectra. The synthesized samples (Fig. 4(a,b)) display a strong absorption in visible region owing to the bandgap transition of CuZnWO₄ semiconductor indicating their probable application as photocatalysts. The CuZnWO₄ shows an absorption edge at 530 nm and the rGO loaded CuZnWO₄ shows the high absorption at 545 nm compared than CuZnWO₄(530 nm). The calculated band-gap energies of 2.27 and 2.18 eV, corresponding to the CuZnWO₄ and CuZnWO₄-rGO, respectively. It clearly shows the CuZnWO₄-rGO composite parades high catalytic activity than CuZnWO₄ under visible light due to the lowest band-gap of 2.18 eV. The trapping and recombination of electron holes is playing a vital role in photocatalytic activity, where analyzed by photoluminescence spectra in Fig. 4(d). The PL spectra of CuZnWO₄ and CuZnWO₄-rGO are shown in Fig.4(d). it possesses a green-blue spectrum with an extreme intensity at 411 nm and CuZnWO₄-rGO shows lower intensity than CuZnWO₄[29,30]. The results demonstrate the recombination capability rate of electrons as well as holes is inhibited considerably in CuZnWO₄-rGO composite.

3.4. Scanning Electron Microscope (SEM)
The SEM images of CuZnWO$_4$ and CuZnWO$_4$-rGO are revealed in Fig. 5. CuZnWO$_4$ shows a composed structure of plates and rod-like/crystal structure (Fig. 5(a and b))[31]. CuZnWO$_4$-rGO revealed the plate as well as improved rod-like structure(Fig. 5(c and d)). The closely crammed surface structure of the CuZnWO$_4$-rGO composite particles is beneficial for effectual charge transporter separation[32,33].

3.6. Photocatalytic activity

The photocatalytic efficiency of the synthesized samples is examined by degradation of organic pollutant (methylene blue (MB)) under visible light irradiation. Fig. 6 demonstrate the MB dye degradation using pure CuZnWO$_4$ and CuZnWO$_4$/rGO composite. The MB aqueous solution displayed the absorbance band at $\lambda = 661$ nm is shown in Fig. 6(a,b). The initial absorbance peak intensity is gradually decreased with the increment of irradiation time from 0 min – 80 min owing to the disintegration of MB dye on the catalyst surface. The pure CuZnWO$_4$ shows 51 % degradation of MB dye for 80 min under visible light, but the composite shows 73 % of degradation owing to the existence of rGO, which improve the catalytic performance of CuZnWO$_4$. The efficiency of the synthesized materials is compared with previous reports given in Table-1.

MB degrade and form H$_2$O, CO$_2$ and some other inorganic contaminants after photocatalytic degradation. The probable degradation mechanism of MB dye by CuZnWO$_4$ and its composite is clearly clarified in following equations. Initially the CuZnWO$_4$ is irradiated by visible light, it captivates the energy approximately equal/higher than its band-gap to enable the development of electron-hole pairs. The electron from the valance band (VB) moved to the vacant conduction band (CB), results show holes formation in the VB and electrons in CB. The oxygen molecules are reduced by highly exited electrons and form a super oxide radical ($^\cdot$O$_2^-$) and also, water molecules oxidized by fast-responsive electron holes to form hydroxy radicals ($^\cdot$OH). $^\cdot$O$_2^-$ and $^\cdot$OH radicals are fully responsible for the photocatalytic degradation of organic pollutants into CO$_2$, H$_2$O and some other inorganic contaminants as a product [34,35].

\[
\text{CuZnWO}_4 + h\nu \text{ (visible light)} \rightarrow \text{CuZnWO}_4 \left( h^+ + e^- \right) \quad \quad (2)
\]

\[
r\text{GO} + h\nu \rightarrow e^- \quad \quad (3)
\]

\[
e^- + O_2 \rightarrow ^\cdot O_2^- \quad \quad (4)
\]
\[ O_2^- + H_2O \rightarrow OH^- \quad (5) \]
\[ h^+ + H_2O \rightarrow OH^- \quad (6) \]
\[ O_2^-/OH^-/h^- + MB \rightarrow \text{degradation products} (CO_2 + H_2O) \quad (7) \]

**Photocatalytic reaction pathway of MB**

Fig. 7 shows MB’s chemical structure and the pathway of the photocatalytic reaction. In photocatalytic degradation, n-dealkylation of dyes holding auxochrome alkylamine groups play a key role. When part of a methyl group degrades, the color of MB solutions has become frailer (color less) and hypochromic change takes place. Therefore, Methylene blue demethylation appears at first as defined in the pathway, and finally MB depredated to CO\(_2\), H\(_2\)O and some other inorganic components [36,37].

Fig. 8(a) shows the degradation efficiency of the synthesized samples. To understand the quantitative kinetics of the MB dye degradation reaction, the degradation data is fit by first order kinetics model, using eq(8).

\[- \ln \left( \frac{C_t}{C_0} \right) = Kt \quad (8)\]

Where k is min\(^{-1}\)rate constant of the reaction and t is min are the seeming first-order rate constants and treatment time, C\(_0\) – initial concentration of dye and C\(_t\)s remaining concentration of dye at each period. model fitting-plots and consistent k standards are revealed in Fig. 8(a,b). we calculate the seeming reaction-rate constant from slope of the plot ofln(C\(_0\)/C) Vs irradiation time. From these plots, we attain the synthesized samples rate constant, the data are shown in Fig. 8(c), the result confirmed that CuZnWO\(_4\)-rGO have higher catalytic degradation efficiency than CuZnWO\(_4\). The attained seeming rate constant (k) values are 0.0151 and 0.0083 for CuZnWO\(_4\)-rGO and CuZnWO\(_4\) respectively.

**3.7. Electrochemical studies**

The electrochemical properties of CuZnWO\(_4\) and CuZnWO\(_4\)-rGO composite are examined by cyclic voltametric (CV) technique. In a three-electrode cell system, Ag/AgCl is used as a reference electrode, platinum wire as a counter electrode and the synthesized samples as a working electrode in 3 M KOH aqueous electrolyte solution. Fig. 9(a) and (b) shows the CV
curves of CuZnWO$_4$ and CuZnWO$_4$/rGO composite electrodes at various scan rates in between the potential range from 0 to 0.6 V. All CV curves display a pair of strong redox-peaks, revealing the pseudo-capacitive features of the synthesized electrode thus the strong redox peaks are mostly governed by reversible Faradic redox process of M$^{2+}$/M$^{3+}$ [38]. According to the CV curve, current response of electrode material will increase with the increases of scan rates. The perfect quasi-rectangular CV shape of the electrodes remain constant at high scan rate, it proposes perfect capacitive behaviour. The potential of oxidation and reduction peaks are moved towards more positive and move negative respectively, which is mostly associated with the internal resistance of the electrode. The CV curves of CuZnWO$_4$/rGO composite shows higher current density and specific surface area than CuZnWO$_4$ due to the synergetic effects in between rGO and CuZnWO$_4$, which enhance the electro chemical performance and specific capacitance[39].

Galvanic charge discharge (GCD) measurements of the synthesized samples are conducted at various current density ranges between 4 and 20 Ag$^{-1}$ (Fig. 9(c) and (d)). CuZnWO$_4$/rGO composite offer higher Cs (480 F g$^{-1}$) than CuZnWO$_4$ electrode (15 F g$^{-1}$) at the same current-density of 4 Ag$^{-1}$. The CuZnWO$_4$/rGO composite shows superior electrochemical performance than pristine CuZnWO$_4$ electrode due to the synergetic effect of electroactive and porous rGO sheets[40], which boost the number of oxidation states, accessible interaction shells and enables the kinetics of ions and electrons transference from the electrolyte. The specific capacitance (Cs) or charge/discharge time decreases with increasing energy density, due to the fact of that the electrolyte-ions are unable to entirely access the internal surface area of the active-materials for charge-storing owing to the decreased diffusion time at high energy density. The Cs is calculated from GCD using the following equation[41–43]

$$C_s = \frac{I \times \Delta t}{\Delta V \times m} \quad (8)$$

Where, Cs - specific capacitance, I – response current, $\Delta t$ - discharging time, $\Delta V$ - Potential window, and m - mass (g) of active material. The calculated specific capacitance (Cs) of 480, 465, 340, 295, 276, 252, 248, 243, 240 F g$^{-1}$ at current density of 4, 6, 8, 10, 12, 14, 16, 18, 20 A g$^{-1}$, respectively.

The comparison of GCD curve (Fig.10(a)) is revealed that the CuZnWO$_4$/rGO composite offer higher charging and discharging time than pristine CuZnWO$_4$, due to the high surface area
of rGO based composite [44]. Fig. 10(b) shows the specific capacitance comparison of the synthesized electrode materials. It clearly shows that the composite has higher specific capacitance than CuZnWO₄. Amazingly, the increasing cyclability of CuZnWO₄/rGO composite electrode is shown in Fig. 10(c). The CuZnWO₄/rGO offers cyclic retention of 127% at 20 A g⁻¹ due to the continuous charging/discharging process raises the wettability of CuZnWO₄/rGO, where enhanced the diffusion of electrolyte ions to the electrode material. The continuous activation of CuZnWO₄/rGO composite during charging/discharging process that increase the interaction between electrode and electrolyte ions, resulting to increases specific capacitance (Cs increases with number of charging/discharging cycles)[45–47]. Electrochemical impedance spectra (EIS) of the synthesized electrode materials is illustrated in Fig. 10(d). The internal and external resistance of the synthesized electrode materials and electrode/electrolyte are estimated via open circuit potentials (OCP) from 0.1 to 105 Hz respectively. In Fig. 10(d) shows the Nyquist plot and circuit diagram of CuZnWO₄ and CuZnWO₄/rGO composite. Pristine CuZnWO₄ shows more resistance than the CuZnWO₄/rGO composite from this EIS spectra we conclude that the composite offers higher electrochemical performance and specific capacitance due to the lower internal resistance.

4. Conclusion

In the present work, we synthesized a nano-structured bimetallic tungstate CuZnWO₄ and its composite with rGO via hydrothermal method. The synthesized materials are used as a catalyst for photocatalytic activity and electrode for SCs. CuZnWO₄/rGO shows better photocatalytic activity and electrochemical performance than pristine CuZnWO₄ due to efficient interaction of rGO, the high surface area of rGO is captured more electrons for efficient degradation of organic pollutants with degradation efficiency of 73% (CuZnWO₄/rGO). The electrochemical performance of the synthesized composite electrode (CuZnWO₄/rGO) shows the Cs 480 F g⁻¹ at 4 A g⁻¹ in aqueous 6 M KOH electrolyte respectively, the electrode reveals enhanced cyclability of 127% at 20 A g⁻¹ after 5000 cycles due to the increasing of interaction between electrode and electrolyte. The synergetic effect of CuZnWO₄ and rGO lead to high storage capacity and outstanding cyclability. The above results confirmed that the synthesized material is a potential candidate for photocatalytic and supercapacitor application.
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Reference

1. J. Yesuraj and S. A. Suthanthiraraj, J. Mol. Struct. 1181, 131 (2019).
2. K. T. G. Carvalho, O. F. Lopes, D. C. Ferreira, and C. Ribeiro, J. Alloys Compd. 797, 1299 (2019).
3. S. M. Alshehri, J. Ahmed, T. Ahamad, N. Alhokbany, P. Arunachalam, A. M. Al-Mayouf, and T. Ahmad, J. Sol-Gel Sci. Technol. 87, 137 (2018).
4. S. Chen, G. Yang, Y. Jia, and H. Zheng, ChemElectroChem 3, 1490 (2016).
5. K. Adib, M. Rahimi-Nasrabadi, Z. Rezvani, S. M. Pourmortazavi, F. Ahmadi, H. R. Naderi, and M. R. Ganjali, J. Mater. Sci. Mater. Electron. 27, 4541 (2016).
6. V. Faka, S. Tsoumachidou, M. Moschogiannaki, G. Kiriakidis, I. Poullos, and V. Binas, J. Photochem. Photobiol. A Chem. 406, 113002 (2021).
7. U. M. García-Pérez, A. Martínez-De La Cruz, and J. Peral, Electrochim. Acta 81, 227 (2012).
8. J. Ahmed, T. Ahamad, N. Alhokbany, B. M. Almaswari, T. Ahmad, A. Hussain, E. S. S. Al-Farraj, and S. M. Alshehri, ChemElectroChem 5, 3938 (2018).
9. S. Kundu, L. Ma, Y. Chen, and H. Liang, J. Photochem. Photobiol. A Chem. 346, 249 (2017).
10. S. M. Alshehri, J. Ahmed, A. M. Alzahrani, and T. Ahamad, New J. Chem. 41, 8178 (2017).
11. A. A. G. Santiago, R. L. Tranquilin, M. S. Li, E. Longo, F. V. Motta, and M. R. D. Bomio, Mater. Chem. Phys. 258, 123991 (2021).
12. H. He, Z. Luo, Z. Y. Tang, and C. Yu, Appl. Surf. Sci. 490, 460 (2019).
13. M. Liu, L. Gan, W. Xiong, F. Zhao, X. Fan, D. Zhu, Z. Xu, Z. Hao, and L. Chen, Energy and Fuels 27, 1168 (2013).
14. M. N. Rantho, M. J. Madito, and N. Manyala, J. Alloys Compd. 819, 152993 (2020).
15. R. D. Kumar, Y. Andou, and S. Karuppuchamy, J. Alloys Compd. 654, 349 (2016).
16. H. Naderi, H. Sobati, A. Sobhani-Nasab, M. Rahimi-Nasrabadi, M. Eghbali-Arani, M. R. Ganjali, and H. Ehrlich, ChemistrySelect 4, 2862 (2019).
17. R. Dhipil Kumar and S. Karuppuchamy, J. Alloys Compd. 674, 384 (2016).
18. J. Jo, S. Lee, J. Gim, J. Song, S. Kim, V. Mathew, M. H. Alfaruqi, S. Kim, J. Lim, and J.
Kim, R. Soc. Open Sci. 6, (2019).
19. M. Mosleh and K. Taherinejat, J. Mater. Sci. Mater. Electron. 27, 10510 (2016).
20. C. Wei, Y. Huang, X. Zhang, X. Chen, and J. Yan, Electrochim. Acta 220, 156 (2016).
21. L. Xu, X. Wang, M. L. Xu, B. Liu, X. F. Wang, S. H. Wang, and T. Sun, Ultrason. Sonochem. 61, 104815 (2020).
22. K. Qureshi, M. Z. Ahmad, I. A. Bhatti, M. Zahid, J. Nisar, and M. Iqbal, J. Mol. Liq. 285, 778 (2019).
23. K. S. Samantaray, S. Sahoo, and C. S. Rout, Am. J. Eng. Appl. Sci. 9, 584 (2016).
24. S. Muthamizh, R. Suresh, K. Giribabu, R. Manigandan, S. P. Kumar, S. Munusamy, L. Vijayalakshmi, A. Stephen, and V. Narayanan, AIP Conf. Proc. 1591, 508 (2014).
25. B. Kavitha and R. Karthiga, 11, 57 (2020).
26. W. Zhang, J. Yin, F. Min, L. Jia, D. Zhang, Q. Zhang, and J. Xie, J. Alloys Compd. 690, 221 (2017).
27. Z. Amouzegar, R. Naghizadeh, H. R. Rezaie, M. Ghahari, and M. Aminzare, Ceram. Int. 41, 8352 (2015).
28. N. Hu, Z. Yang, Y. Wang, L. Zhang, Y. Wang, X. Huang, H. Wei, L. Wei, and Y. Zhang, Nanotechnology 25, (2014).
29. Y. Tang, N. Rong, F. Liu, M. Chu, H. Dong, Y. Zhang, and P. Xiao, Appl. Surf. Sci. 361, 133 (2016).
30. S. Roddaeng, P. Promvonge, and R. Anuwattana, MATEC Web Conf. 192, 8 (2018).
31. P. V. Adhyapak, A. D. Bang, P. More, and N. R. Munirathnam, RSC Adv. 8, 34035 (2018).
32. S. Zhong, C. Li, M. Shen, C. Lv, and S. Zhang, J. Mater. Res. Technol. 8, 1849 (2019).
33. A. K. Adepu, S. Goskula, S. Chirra, S. Siliveri, S. R. Gujjula, and V. Narayanan, RSC Adv. 9, 24368 (2019).
34. M. Thiruppathi, K. Leeladevi, C. Ramalingan, K. C. Chen, and E. R. Nagarajan, Mater. Sci. Semicond. Process. 106, 104766 (2020).
35. C. P. Goyal, D. Goyal, V. Ganesh, N. S. Ramgir, M. Navaneethan, Y. Hayakawa, C. Muthamizhchelvan, H. Ikeda, and S. Ponnusamy, Phys. Solid State 62, 1796 (2020).
36. X. Q. Wang, S. F. Han, Q. W. Zhang, N. Zhang, and D. D. Zhao, MATEC Web Conf. 238, (2018).
37. R. S. Dariani, A. Esmaeili, A. Mortezaali, and S. Dehghanpour, Optik (Stuttg). 127, 7143
38. R. Dhilip Kumar, Y. Andou, M. Sathish, and S. Karuppuchamy, J. Mater. Sci. Mater. Electron. 27, 2926 (2016).
39. J. Tang, J. Shen, N. Li, and M. Ye, *Facile Synthesis of Layered MnWO4/reduced Graphene Oxide for Supercapacitor Application* (2016).
40. M. Mitra, S. T. Ahamed, A. Ghosh, A. Mondal, K. Kargupta, S. Ganguly, and D. Banerjee, ACS Omega 4, 1623 (2019).
41. X. Xing, Y. Gui, G. Zhang, and C. Song, Electrochim. Acta 157, 15 (2015).
42. J. Chu, X. Li, Q. Li, J. Ma, B. Wu, X. Wang, R. Zhang, M. Gong, and S. Xiong, High Perform. Polym. 32, 258 (2020).
43. K. Seevakan, A. Manikandan, P. Devendran, Y. Slimani, A. Baykal, and T. Alagesan, Ceram. Int. 44, 20075 (2018).
44. A. Iakunkov, V. Skrypnychuk, A. Nordenström, E. A. Shilayeva, M. Korobov, M. Prodana, M. Enachescu, S. H. Larsson, and A. Vtalyzin, Phys. Chem. Chem. Phys. 21, 17901 (2019).
45. A. E. Elkholy, A. S. Dhmees, F. E. T. Heakal, and M. A. Deyab, New J. Chem. 43, 1987 (2019).
46. M. Ramadan, A. M. Abdellah, S. G. Mohamed, and N. K. Allam, Sci. Rep. 8, 1 (2018).
47. J. Zhou, J. Lian, L. Hou, J. Zhang, H. Gou, M. Xia, Y. Zhao, T. A. Strobel, L. Tao, and F. Gao, Nat. Commun. 6, (2015).
48. M. Mousavi, A. Habibi-Yangjeh, and M. Abitorabi, J. Colloid Interface Sci. 480, 218 (2016).
49. R. Salimi, A. A. Sabbagh Alvani, N. Naseri, S. F. Du, and D. Poelman, New J. Chem. 42, 11109 (2018).
50. A. M. Raba-Páez, J. O. João, C. A. Parra-Vargas, E. C. Paris, and M. Rincón-Joya, Mater. Today Commun. (2020).
51. W. Zou, L. Zhang, L. Liu, X. Wang, J. Sun, S. Wu, Y. Deng, C. Tang, F. Gao, and L. Dong, Appl. Catal. B Environ. 181, 495 (2016).
52. H. Wang, X. Yuan, H. Wang, X. Chen, Z. Wu, L. Jiang, W. Xiong, and G. Zeng, Appl. Catal. B Environ. 193, 36 (2016).
53. M. Rahimi-Nasrabadi, S. M. Pourmortazavi, M. Aghazadeh, M. R. Ganjali, M. S. Karimi, and P. Novrouzi, J. Mater. Sci. Mater. Electron. 28, 3780 (2017).
54. S. Ameen, H. K. Seo, M. Shaheer Akhtar, and H. S. Shin, Chem. Eng. J. 210, 220 (2012).
55. B. G. S. Raj, J. Acharya, M. K. Seo, M. S. Khil, H. Y. Kim, and B. S. Kim, Int. J. Hydrogen Energy 44, 10838 (2019).
56. R. Dhilip Kumar and S. Karuppuchamy, Ceram. Int. 40, 12397 (2014).
57. S. M. Pourmortazavi, M. Rahimi-Nasrabadi, M. S. Karimi, and S. Mirsadeghi, New J. Chem. 42, 19934 (2018).
58. D. P. Ojha, H. P. Karki, J. hee Song, and H. J. Kim, Chem. Phys. Lett. 712, 83 (2018).
59. U. Nithiyanantham, S. R. Ede, S. Anantharaj, and S. Kundu, Cryst. Growth Des. 15, 673 (2015).
Table caption
Table – 1: Comparison of Dye degradation efficiency with previous reported literatures
Table – 1: Comparison of the electrochemical performance with previous reported literatures

Figure caption

Fig. 1. Graphical abstract

Fig. 2. XRD pattern: a) CuZnWO4 and b) CuZnWO4/rGO

Fig. 3. FTIR spectra: a) CuZnWO4 and b) CuZnWO4/rGO

Fig. 4. (a,b) UV-DRS absorption and transmission spectrum and (c) photoluminencesce spectram and d) tauclplot

Fig. 5. SEM images: a,b) CuZnWO4 and c,d) CuZnWO4-rGO low and high magnification respectively

Fig. 6. Photocatalytic dye degradation: a) CuZnWO4, b) CuZnWO4/rGO and c) Comparison of methylene blue degradation efficiency of CuZnWO4 and CuZnWO4/rGO under visible light

Fig. 7. Ln C/Co vs. irradiation time for photocatalytic degradation of MB dye

Fig. 8. Mechanism of methylene blue dye degradation

Fig. 9. Cyclic voltammograms at various scan rates from 5 to 100 mV.s⁻¹ a) CuZnWO4 and b) CuZnWO4/rGO, GCD at various current densities from 4 to 20 A. g⁻¹ c) CuZnWO4 and d) CuZnWO4.

Fig. 10. a) GCD comparison of CuZnWO4 and CuZnWO4/rGO at6 Ag⁻¹, b) Comparison specific capacitance Vs current density c) Cyclability and cumibic efficiency ofCuZnWO4/rGO d) Nyquest plots

| Catalyst                        | Pollutant | Efficiency (%) | Time (Min) | Reference |
|---------------------------------|-----------|----------------|------------|-----------|
| g-C3N4/Fe3O4/AgCl              | RhB       | 49.5           | -          | [48]      |
| Ag-CuWO4/WO3                   | MB        | 51             | 180        | [49]      |
| CuO with CuWO4                 | RhB       | 20             | 160        | [50]      |
| o-Cu2O–rGO                     | MB        | 72             | 160        | [51]      |
| CNQD-utg-C3N4                  | MO        | 70             | 160        | [52]      |
| TiO2                            | MB        | 50             | 60         | [53]      |
| polyaniline/graphene           | RhB       | 56             | 180        | [54]      |
| CuZnWO4/rGO                    | MB        | 80 min         |            | This Work |
### Table-2

| Electrode material | Electrolyte           | Specific capacitance               | Reference |
|--------------------|-----------------------|------------------------------------|-----------|
| CoWO<sub>4</sub>   | 2 M H<sub>2</sub>SO<sub>4</sub> | 378 F/g at 2 mV/s                  | [5]       |
| MnWO<sub>4</sub>   | 1 M Na<sub>2</sub>SO<sub>4</sub> | 324 F/g at 1 mA cm<sup>2</sup>    | [55]      |
| CuWO<sub>4</sub>   | 0.1 M KCl with 1mM [Fe(CN)<sub>6</sub>]<sup>3/-4-</sup> | 77 F/g                             | [56]      |
| CuWO<sub>4</sub>   | 2 M KOH               | 302.40 mAh/g at 1 A/g              | [20]      |
| Ni-WO<sub>3</sub>  | 2 M KOH               | 171.28 F/g at 0.25 A/g             | [15]      |
| CWO-NPs            | 1 M KOH               | 230 F/g at 5 mV/s                  | [8]       |
| NiWO<sub>4</sub> NPs | 3 M H<sub>2</sub>SO<sub>4</sub> | 468 F/g at 2 mV/s                  | [57]      |
| FWO/gCN            | 2 M KOH               | 357 F/g at 5 mV/s                  | [58]      |
| NiWO<sub>4</sub>   | 2 M KOH               | 173 F/g at 5 mV/s                  | [59]      |
| CuZnWO<sub>4</sub>/rGO | 6 M KOH               | 480 F/g at 6 A/g                   | This Work |

![Fig. 1](image-url)
Fig. 2

- Red line: CuZnWO$_4$
- Blue line: CuZnWO$_4$-rGO

(a) and (b) show the X-ray diffraction patterns for CuZnWO$_4$ and CuZnWO$_4$-rGO, respectively.
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7
Fig. 8
Fig. 9
Fig. 10