Hydrogen Peroxide Assisted Photocatalytic Dye Degradation Over Reduced Graphene Oxide Integrated ZnCr_2O_4 Nanoparticles

Kartik Tantubay

The University of Burdwan

Piu Das

The University of Burdwan

Moni Baskey (Sen) (✉ moni.baskey@gmail.com)

University of Burdwan <https://orcid.org/0000-0003-2031-6929>

Research Article

Keywords: ZnCr_2O_4 -rGO, nanocomposite, catalytic activity, methylene blue, hydrogen peroxide.

Posted Date: September 9th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-794253/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License. [Read Full License](#)

Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on October 18th, 2021. See the published version at <https://doi.org/10.1007/s11356-021-17105-1>.

Abstract

Zinc chromite nanoparticles (NPs) and zinc chromite-reduced graphene oxide ($\text{ZnCr}_2\text{O}_4\text{-rGO}$) nanocomposite have been synthesized by the combined effect of reflux condensation and calcination process. The structural properties were characterised by X-ray diffraction (XRD), Fourier transform infrared (FTIR), UV-visible studies etc. Structural morphology was investigated by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) that indicates the formation of particles in nanometre regime. The catalytic effects of synthesized materials were studied in presence of visible light assisted by hydrogen peroxide (H_2O_2) and they show excellent photo activity which supports the band gap value and photoluminescence outcome. The presence of the elements Zn, Cr, O and C has been confirmed by Energy dispersive X-ray spectroscopy (EDX) images which show the purity of the synthesized products.

Introduction

The heterogeneous photocatalyst gives great promise for environmental contaminants elimination by transfer photon energy into chemical energy (Nguyen et al. 2016; Kalisamy et al. 2020). The photocatalytic treatment for eradication of hazardous environmental pollutants, such as, various organic dyes, chemical compounds etc. is one of the most efficient and economical concerns. These pollutants egress from industries like textile, paper, food, cosmetic, pharmaceutical industries and contaminate water (Dong et al. 2015; Shang et al. 2014). So, removal of these pollutants from water is very important for living beings. Graphene based nanocomposites gives auspicious results for the removing of the contaminants by catalytic (Anshuman et al. 2018; Tantubay et al. 2020), photocatalytic (Kocijan et al. 2021; Das et al. 2018; An X and Yu JC 2011), adsorption (Chen et al. 2013; Dubey et al. 2015) and other process due to its unique properties like large surface area (Singh et al. 2021), sp^2 hybridized carbon network (Gao et al. 2018), high electrical conductivity (Rahaman et al. 2020) and electron mobility (Guptaa et al. 2020) etc. There are several graphene based photocatalyst rGO-TiO_2 (Yu et al. 2017), rGO-ZnO (Kumar et al. 2021), rGO-CuS/ZnS (Das et al. 2021), rGO-CuO (Gusain et al. 2016), rGO-NiO (Nafiey et al. 2017), rGO-Ag (Sen and Ghosh 2017) etc. for removing of organic dyes like methylene blue, rhodamine B, eosin-Y, congo red, crystal violet etc. by using UV or Visible light. But there are very few spinal nanocomposites reported for the removal of organic dyes from contaminant water.

There are much more spinel nanomaterials which showed their enhanced catalytic activities after combined up with graphene or reduced graphene oxide (Padhi et al. 2017; Amer et al. 2017; Gnanamoorthy et al. 2020; Krishnan et al. 2020). But Zinc chromite (ZnCr_2O_4) is a less studied material which behaves as nanocatalyst in visible light irradiation and also there is no any report about the synthesis of graphene or reduced graphene oxide functionalized ZnCr_2O_4 nanocomposite. Being a mixed oxide, it has significant role in material science for its physical and chemical properties suitable for various applications. There are fewer literature surveys as describes in Table 1 about the applications of ZnCr_2O_4 such as, photocatalysis process for removal of various organic dyes (Dumitru et al. 2018; Sabet and Jahangiri 2018), catalytic application for thermal decomposition (Wang et al. 2020) and sensing property for explosive nitro compounds (Ghosh et al. 2018), humidity sensing (Pokhrel et al. 2003) but no one synthesize the low dimensional ZnCr_2O_4 nanomaterials which can response in visible light to degrade organic dye. There are several methods for synthesis of ZnCr_2O_4 nanomaterials, such as, thermal conversion (Dumitru et al. 2018), hydrothermal process (Sabet and Jahangiri 2018), sol-gel process

(Choudhary et al. 2017), combustion process (Kumar et al. 2017) reflux process (Tajizadegan et al. 2016) etc. Out of these, refluxed followed by calcination is very simple and more cost- effective method to synthesis different nanomaterials.

Here, in this paper, about 4–7 nm ZnCr_2O_4 NPs on reduced graphene oxide (rGO) surface have been synthesized by simple reflux method followed by calcination and then after characterization by XRD, FTIR, UV-Vis, FESEM, TEM, PL studies the visible light active photocatalytic activity for the degradation of methylene blue organic dye has been investigated.

Table 1
Summary of photocatalytic performance of ZnCr_2O_4 nanomaterials reported in recent paper till date

photocatalyst	Amt. of sample used	Dye used	Dye conc & amt.	Irradiation light source	Irradiation time	% of degradation	Reference (year)
ZnCr_2O_4 NPs	400 mg L^{-1}	Methylene blue	2.46 ppm & 400 ml	300 W medium-pressure Hg lamp	120 min	87	(Peng et al. 2008)
$\text{ZnO-ZnCr}_2\text{O}_4$ nanolayered	4000 mg L^{-1}	Acid orange 10	10.01 ppm & 200 ml	500 W tungsten lamp	180 min.	99	(Thennarasu et al. 2015)
ZnCr_2O_4 Dendrimer	1000 mg L^{-1}	Eriochrome Black T	20 ppm & 50 ml	ultra violet radiation	120 min	91	(Sabet et al. 2018)
$\text{TiO}_2\text{-ZnCr}_2\text{O}_4$ core-shell NPs	1000 mg L^{-1}	Methylene blue	30 ppm & 50 ml	UV lamp (15 W, Philips)	120 min	99	(Salehi et al. 2018)
$\text{ZnS-ZnCr}_2\text{O}_4$ nanohybrid	400 mg L^{-1}	Methyl orange	40 ppm & 100 mL	Tungsten-halogen lamp	105 min	96.88	(Palanisamy et al. 2020)
$\text{ZnCr}_2\text{O}_4\text{-rGO}$	200 mg L^{-1}	Methylene blue	10 ppm & 50 ml	500 W tungsten lamp	70 min	96	Present work

Materials And Methods

Materials

Zinc sulphate [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$] (Merck), chromium nitrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] (Merck), polyvinyl pyrrolidone (PVP) (LOBA), ultrafine graphite powder (Sigma-Aldrich), conc. sulfuric acid (Merck) conc. hydrochloric acid (Merck), potassium permanganate (Merck), liquor ammonia (Merck), hydrogen peroxide, acetone, ethanol, doubled distilled water, methylene blue dye.

Preparation Of Go

Graphene Oxide (GO) was prepared following the Modified Hummers method (William et al. 1958). Using this method at first 1g natural flake graphite powder was taken in 500 ml of beaker and added 23 ml Concentrated H_2SO_4 to it. Then the mixture was subjected to magnetic stirrer for 48 hours. After stirring potassium permanganate was added slowly in ice cold condition and the color has been changed from greenish to brown. Then, the whole dispersion was transferred into ice cold water and after that hydrogen peroxide was added to make the complete reduction and the color turned from brown to pale yellow. Centrifugation was done to collect the precipitate, then washed several times with 10% HCl followed by distilled water. Finally, the precipitate was obtained as GO.

Synthesis Of Zncro-rgo Spinel Nanoparticle

ZnCr_2O_4 -rGO nanocomposites have been synthesized using graphene oxide (GO) sheet as growing substrate in simple chemical process. At first 0.364 g GO was dispersed in 120 mL distilled water and sonicated for 40 minutes for clear dispersion. 20 mL of 0.35 (M) zinc sulphate and 20 mL 0.70 (M) chromium nitrate solution was added separately to this GO dispersion with continuous stirring condition. The total solution is stirred for next 20 minutes and then pH-10 was adjusted by adding liquor ammonia drop wise. Then the whole dispersion was subjected to reflux for 11 hours after stirring for 3 hours at 80°C . The obtained product was filtered, washed with distilled water and ethanol and finally dried at 80°C under vacuum condition as shown in Scheme. 1. Bare ZnCr_2O_4 nanoparticles was synthesized using polyvinylpyrrolidone (PVP) as a stabilizer instead of GO. The two dried samples were heated for 3 hours at 500°C for calcination.

Characterization Techniques

The crystal structures of the composites were determined by the X- Ray Diffractometer BRUKER D8 ADVANCE and nature of the chemical bonding was investigated by Fourier Transform Infrared (FTIR) study using SHIMADZU IR Prestige-21. UV-Vis study and the photocatalytic activity studies were carried out by SHIMADZU UV- 1800 spectrophotometer. The size and the morphological study of these nanocomposites were investigated by the Scanning Electron Microscope (Model SIGMA-300). Photoluminescence (PL) study was done by Hitachi F-4500 spectrofluorimeter.

Photocatalytic Activity Study

The photocatalytic performances of the two powdered samples ZnCr_2O_4 NPs and ZnCr_2O_4 -rGO nanocomposites were investigated by the degradation of methylene blue (MB), an organic dye under a visible

light irradiation. 10 mg of each sample was added to 50 ml MB dye solution (2.5 mg/L) separately and the mixture was stirred for 20 min to maintain adsorption-desorption equilibrium in dark environment. After 30 minutes of adsorption–desorption process H₂O₂ was added to it and then exposed to visible light 500 W xenon lamp powers with constant stirring. UV-Vis absorption data were taken continuously after certain intervals of time, and it was found that the deep blue color of MB gradually disappears. Measuring the absorbance intensity during the photocatalytic degradation process, degree of degradation was calculated using this relation:

$$D\% = \frac{A_o - A_t}{A_o} \times 100 \dots\dots\dots (Eq. 1)$$

Results And Discussion

X-ray diffraction (XRD) patterns were collected to know the crystallographic structure of the synthesized samples ZnCr₂O₄ NPs and ZnCr₂O₄-rGO nanocomposite presented in the Fig. 1a. The characteristic peaks appeared at 30.2°, 35.5°, 43.5°, 53.8°, 57.4°, 63.4°, 75.2° corresponds to the lattice planes of (220), (311), (400), (422), (511), (440), (620) respectively. It is observed that all the XRD diffraction peaks for pure ZnCr₂O₄ sample recorded in the JCPDS – 22-1107 are in a perfect match with the diffraction patterns of ZnCr₂O₄ in the composite material and also in ZnCr₂O₄ nanoparticles which confirms the formation of ZnCr₂O₄-rGO nanocomposite.

FTIR spectra of the two synthesized sample ZnCr₂O₄-rGO nanocomposite and GO were recorded from 4000 cm⁻¹ to 400 cm⁻¹. In Fig. 1(b), GO has the characteristic peaks at 3395, 1725, 1620, 1053, 1230 cm⁻¹ for the corresponding O-H, C = O, C = C, C-O stretching and C-O-C bending respectively (Sharma et al 201; Sudesh et al. 2013). But in the nanocomposite sample the presence of two strong bands at 520 cm⁻¹ and 623 cm⁻¹ indicate the stretching vibrations of Cr-O and Zn-O bonds respectively. At the same time, the appearance of the peaks located at around 1121 (C-O stretching) and 1627 (C = C) cm⁻¹ and low intensity of the peak due to O-H stretching confirms the formation of the reduced graphene oxide along with the ZnCr₂O₄ nanoparticles.

The absorption spectra of the ZnCr₂O₄-rGO nanocomposite was recorded from 200 to 800 nm wavelength range as shown in Fig. 2. The peaks at around 270 nm and 355–390 nm can be assigned for the π-π* transition of aromatic C-C bond in graphene network and octahedral Cr³⁺ (d³) ions. The hump arises near the visible region can be attributed to band gap absorption of ZnCr₂O₄ nanoparticles which is quite left shifted than the reported literature (Naz et al. 2016; Abdullah et al. 2016). The absorption band gap can be estimated using the following Tauc relation (Zanatta et al. 2019):

$$\alpha h\nu = A(h\nu - E_g)^n$$

2
.....

where A is a constant and E_g is the absorption band gap of the material, n is a number which indicates the nature of electronic transition between valance band and conduction band, which have the values 1/2, 2, 3/2, and 3 corresponding to the allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions,

respectively. It is well known that, ZnCr_2O_4 responses UV light but from the above equation, the plot of $(\alpha h\nu)^2$ vs. $h\nu$ will give a divergence at an energy value E_g . The estimated band gap value from the plot for ZnCr_2O_4 -rGO nanocomposite can be obtained by extrapolating the straight line to the energy axis at $\alpha = 0$. The linear part shows that the mode of transition in this nanocomposite is direct in nature and the calculated band gap value was found to be 2.82 eV which is less than that of reported value of virgin ZnCr_2O_4 nanoparticles. This might be due to the strain comes about the combination of graphene with nanoparticles for the synthesis of ZnCr_2O_4 -rGO nanocomposite.

The morphology of virgin ZnCr_2O_4 and ZnCr_2O_4 -rGO nanocomposite are analysed by transmission electron microscopy. Virgin ZnCr_2O_4 forms by agglomeration of small particles around 15–20 nm as shown in Fig. 3a. The average particle size of ZnCr_2O_4 NPs in the composite [Fig. 3b] is smaller than that of virgin ZnCr_2O_4 NPs which is due to presence of rGO surface. From the Fig. 3c it is clearly shown that the ZnCr_2O_4 NPs are spread throughout the rGO sheet and the average particle size is approximately 4–7 nm [Fig. 3d] which is proven by particle size distribution curve as shown in Fig. 3e.

The EDX study of the synthesized samples has been carried out from the SEM images. Table 2 described the obtained results from Fig. 3f and Fig. S1 (supporting info) which showed the presence of the elements Zn, Cr, C, O in ZnCr_2O_4 NPs and ZnCr_2O_4 -rGO nanocomposite respectively. Here weight percent of carbon is too much less because of the less amount of GO was used on the synthesis time.

Table 2
EDAX data of bare ZnCr_2O_4 NPs and ZnCr_2O_4 -rGO nanocomposite

Sample	Element	weight %	Atomic %
ZnCr_2O_4	Zn	21.18	9.23
	Cr	40.19	22.01
	O	38.63	68.76
ZnCr_2O_4-rGO	Zn	23.84	10.86
	Cr	42.47	24.32
	O	30.22	56.25
	C	3.46	8.57

The photoluminescence study of the nanomaterial is one of the important characterization by which we can demonstrate the efficiency of migration and transfer of charge carriers and gives information about oxygen vacancies and defects as well as the separation and recombination of photo-induced charge carriers (Gao et al. 2019; Qian et al. 2018). Figure 4c shows the PL spectra for ZnCr_2O_4 and ZnCr_2O_4 -rGO samples with an excitation wavelength of 249 nm. The main emission peak is centered at about 350–450 nm for the two samples. The PL emission intensity decreases slightly from ZnCr_2O_4 to ZnCr_2O_4 -rGO nanocomposite. This suggests the enhanced photocatalytic performance of ZnCr_2O_4 -rGO compared to ZnCr_2O_4 because of lower

recombination rate of photogenerated charge carriers in ZnCr₂O₄-rGO. Because due to presence of rGO sheet in the nanocomposite material the photo-generated electrons from the conduction band (ZnCr₂O₄) moves to the rGO surface and finally reduces the possibility of recombination of electron-hole pairs and photocatalytic activity increases as a result lowering in the PL intensity.

Photocatalytic Study

In order to evaluate the degradation efficiency of the two samples, the irradiation experiment was conducted by H₂O₂-assisted photolysis of MB. In Fig. 4a, it is shown that after visible light irradiation, the degradation of MB dye increases in presence of H₂O₂ but this catalytic reaction enhances in greater extent when NPs is used as catalyst. During the photocatalytic experiments, the nanocatalysts ZnCr₂O₄ and ZnCr₂O₄-rGO achieved 85.48% and 95.69% photo-degradation after 70 minutes of visible light irradiation (Fig. 4a). This is due to the fact that the ZnCr₂O₄-rGO sample has larger surface area than virgin ZnCr₂O₄ NPs because of the decreased size of ZnCr₂O₄ NPs after the addition of GO in nanocomposite. The concentration of MB gradually decreases and this reaction follows pseudo first-order kinetics as shown in Eq. (3),

$$\ln(A_0 / A_t) = kt \text{ Eq. (3)}$$

where, A₀ is the absorbance at t = 0 (initial MB absorbance), A_t the absorbance at time t = t

(Final MB absorbance) and k is rate constant. A linear fit curve was obtained with ln (A₀/A_t) against illumination time and the degradation rate constant was calculated for the sample ZnCr₂O₄ and ZnCr₂O₄-rGO as shown in Table 3.

Table 3
Comparison of the degradation efficiency, the rate constant and relative correlation coefficient of different photo degradation experiments

Experiment	Sample	Degradation %	Rate (min ⁻¹)	R ² value
MB + Light	No	1.26	1.4 X 10 ⁻⁴	0.9611
MB + Light + H ₂ O ₂	No	3.70	5.4 X 10 ⁻⁴	0.7746
MB + Light + H ₂ O ₂ + ZnCr ₂ O ₄	ZnCr ₂ O ₄	85.48	2.28 X 10 ⁻²	0.8956
MB + Light + H ₂ O ₂ + ZnCr ₂ O ₄ -rGO	ZnCr ₂ O ₄ -rGO	95.69	3.36 X 10 ⁻²	0.873

Photocatalytic mechanism

In order to explain the H₂O₂ assisted photocatalytic activity the possible photocatalytic route has been developed in Scheme 2. When the ZnCr₂O₄ NPs and ZnCr₂O₄-rGO nanocomposites photocatalysts were excited with photon energy, the electrons in the valence band (VB) transfer to the conduction band (CB) generating same number of holes in VB as shown in Scheme 2. The photo-generated electrons can form superoxide radical anions (O₂^{•-}) combining with dissolved O₂ and photo-generated holes transform the HO⁻ into HO[•] radical. The recombination of holes (h⁺) and electrons (e⁻) has been considered as an adverse process in

photocatalysis. So, probability of photocatalytic process has been improved by retardation of recombination process or increasing photocatalysis performance in presence of other catalyst. Here H_2O_2 can act as an electron acceptor and thus can form hydroxyl radicals through the following reaction:

First, the direct photolysis of H_2O_2 and generation of free radicals occur after the absorption of visible light (Wong et al. 2003) which is to be expected the dominant rate-enhancing mechanism in this process (Eq. i). Another minor mechanism which has been preferred by Ollis et al. (Ollis et al. 1991) and Ilisz et al. (Ilisz et al. 1998) may partially effect to the rate enhancement, in which H_2O_2 is recommended to be a better electron acceptor than oxygen. This would minimize the possibility of electrons-holes recombination and can generate one hydroxyl radical as shown in Eq ii (Gao et al. 2002), rather than the weaker $\text{O}_2^{\cdot-}$ radical (Eq. v). Finally, these generated radicals ($\text{HO}^{\cdot}$, $\text{O}_2^{\cdot-}$) are the main active species for the degradation of MB dye molecules. In this way of the dual catalysts i.e the nanocomposite and H_2O_2 can affect the degradation of MB dye.

Conclusions

Zinc chromite nanoparticles and graphene hybridised chromite nanocomposite were synthesized by the simple reflux condensation method. Different characterization techniques have been confirmed the formation of these nanomaterial and nanocomposite. Microscopic methods showed that the particle size of zinc chromite NPs in the nanocomposite is smaller than that of bare one. The synthesized nanostructures exhibited excellent photocatalytic activity in presence of H_2O_2 and it is also supported by photoluminescence study and band gap value. In a fixed time limit ZnCr_2O_4 -rGO nanocomposite showed approximately 96% degradation whereas the degradation efficiency is 85 % in case of bare ZnCr_2O_4 NPs. It can be concluded that these nanophotocatalysts could be used extensively for the degradation of pollutants, photocatalytic disinfection and photocatalytic hydrogen generation processes.

Declarations

Acknowledgments

K.T acknowledges Swami Vivekananda Merit-Cum-Means Scholarship (Non-NET Junior Research Fellowship), Higher Education Department, Govt. of West Bengal for financial support and P.D acknowledges Bagati Shib Chandra Banerjee Girls' High School, Hooghly for giving permission to continue her research work. We acknowledge University science instrumentation center (USIC) for SEM facility.

Competing Interests

There are no competing interests.

Ethical approval

All procedures performed in studies involving human participants were in accordance with the ethical standards of the institutional and/or national research committee and with the 1964 Helsinki declaration and its later amendments or comparable ethical standards.

Consent to Participate

All participants voluntarily agreed to participate in this research study.

Consent to Publish

All participants voluntarily agreed to publish their research work in Springer journal.

Authors Contributions

Kartik Tantubay: Writing - original draft, writing - review & editing, conceptualization, methodology, investigation.

Piu Das: Validation, conceptualization, data curation, visualization, formal analysis, funding acquisition.

Moni Baskey Sen: Supervision, writing and conceptualization.

Availability of data and materials

The data that support the findings of this study are available from authors.

References

1. Abdullah OG (2016) Synthesis of single-phase zinc chromite nano-spinel embedded in polyvinyl alcohol films and its effects on energy band gap. *J Mater Sci Mater Electron* 27:12106–12111 doi:10.1007/s10854-016-5361-0
2. Amer AA, Reda SM, Mousa MA, Mohamed MM (2017) Mn_3O_4 /graphene nanocomposites: outstanding performances as highly efficient photocatalysts and microwave absorbers. *RSC Adv* 7:826–839 DOI: 10.1039/c6ra24815b
3. An X, Yu JC (2011) Graphene-based photocatalytic composites. *RSC Adv* 1:1426–1434 <https://doi.org/10.1039/C1RA00382H>
4. Anshuman A, Yarahmadi SS, Vaidhyanathan B (2018) Enhanced catalytic performance of reduced graphene oxide– TiO_2 hybrids for efficient water treatment using microwave irradiation. *RSC Adv* 8:7709–7715 <https://doi.org/10.1039/C8RA00031J>
5. Chen Y, Chen L, Bai H, Li L (2013) Graphene oxide–chitosan composite hydrogels as broad-spectrum adsorbents for water purification. *J Mater Chem A* 1:1992–2001 <https://doi.org/10.1039/C2TA00406B>
6. Choudhary P, Yadav A, Varshney D (2017) Structural and optical studies of nanocrystalline ZnCr_2O_4 and CoCr_2O_4 Spinel. *AIP Conf Proc* 1832: 0500511–0500513 <https://doi.org/10.1063/1.4980284>
7. Das P, Ghosh S, Ghosh R, Dam S, Sen MB (2018) Madhuca longifolia plant mediated green synthesis of cupric oxide nanoparticles: a promising environmentally sustainable material for waste water treatment and efficient antibacterial agent. *J Photochem Photobiol B Biol* 189:66–73 <https://doi.org/10.1016/j.jphotobiol.2018.09.023>
8. Das P, Tantubay K, Ghosh R, Dam S, Sen MB (2021) Transformation of CuS/ZnS nanomaterials to an efficient visible light photocatalyst by ‘photosensitizer’ graphene and the potential antimicrobial activities

- of the nanocomposites. *Environ Sci Pollut Res* 1-14 <https://doi.org/10.1007/s11356-021-14068-1>
9. Dong S, Feng J, Fan M, Pi Y, Hu L, Han X, Liu M, Sun J, Sun J (2015) Recent developments in heterogeneous photocatalytic water treatment using visible-light-responsive photocatalysts: A review. *RSC Adv* 5:14610-14630 <https://doi.org/10.1039/C4RA13734E>
 10. Dubey SP, Nguyen TTM, Kwon YN, Lee C (2015) Synthesis and characterization of metal-doped reduced graphene oxide composites, and their application in removal of *Escherichia coli*, arsenic and 4-nitrophenol. *J Ind Eng Chem* 29:282-288 <https://doi.org/10.1016/j.jiec.2015.04.008>
 11. Dumitru R, Manea F, Păcurariu C, Lupa L, Pop A, Cioabă A, Surdu A, Ianculescu A (2018) Synthesis, characterization of nanosized ZnCr_2O_4 and its photocatalytic performance in the degradation of humic acid from drinking water. *Catalysts* 8:210-225 <https://doi.org/10.3390/catal8050210>
 12. Gao M, Wu X, Qiu H, Zhang Q, Huang K, Feng S, Yang Y, Wang T, Zhao B, Liu Z (2018) Reduced graphene oxide-mediated synthesis of Mn_3O_4 nanomaterials for an asymmetric supercapacitor cell. *RSC Adv* 8:20661–20668 DOI: 10.1039/c8ra00092a
 13. Gao R, Stark J, Bahnmann D, Rabani J (2002) Quantum yields of hydroxyl radicals in illuminated TiO_2 nanocrystallite layers. *J Photochem Photobiol A Chem* 148:387-391 [https://doi.org/10.1016/S1010-6030\(02\)00066-7](https://doi.org/10.1016/S1010-6030(02)00066-7)
 14. Gao W, Lu J, Zhang S, Zhang X, Wang Z, Qin W, Wang J, Zhou W, Liu H, Sang Y (2019) Suppressing photoinduced charge recombination via the lorentz force in a photocatalytic system. *Adv Sci* 6:1901244-1901250 <https://doi.org/10.1002/advs.201901244>
 15. Ghosh D, Dutta U, Haque A, Mordvinova NE, Lebedev OI, Pal K, Gayen A, Seikh MM, Mahata P (2018) Ultra high sensitivity of luminescent ZnCr_2O_4 nanoparticles toward aromatic nitro explosives sensing. *Dalton Trans* 47:5011-5018 DOI: 10.1039/C8DT00047F
 16. Gnanamoorthy G, Ramar K, Ali D, Yadavd VK, Sureshbabu K, Narayanan V (2020) A series of $\text{ZnCo}_2\text{O}_4/\text{rGO}/\text{Pt}$ nanocubes with excellent photocatalytic activity towards visible light. *Chem Phys Lett* 759: 137988-137996 <https://doi.org/10.1016/j.cplett.2020.137988>
 17. Gupta S, Joshia P, Narayan J (2020) Electron mobility modulation in graphene oxide by controlling carbonmelt lifetime. *Carbon* 170:327-337 doi:10.1016/j.carbon.2020.07.073
 18. Gusain R, Kumar P, Sharma OP, Jain SL, Khatri OP (2016) Reduced graphene oxide-CuO nanocomposites for photocatalytic conversion of CO_2 into methanol under visible light irradiation. *Appl Catal B Environ* 181:352-362 DOI:10.1016/j.apcatb.2015.08.012
 19. Ilisz I, Föglein K, Dombi A (1998) The photochemical behavior of hydrogen peroxide in near UV-irradiated aqueous TiO_2 suspensions. *J Mol Catal* 135:55-61 [https://doi.org/10.1016/S1381-1169\(97\)00296-3](https://doi.org/10.1016/S1381-1169(97)00296-3)
 20. Kalisamy P, Lallimathi M, Suryamathi M, Palanivel B, Venkatachalam M, (2020) ZnO -embedded S-doped $\text{g-C}_3\text{N}_4$ heterojunction: mediator-free Z-scheme mechanism for enhanced charge separation and photocatalytic degradation. *RSC Adv* 10:28365-28375 <https://doi.org/10.1039/D0RA04642F>
 21. Kocijan M, Čurković L, Ljubas D, Mužina K, Bačič I, Radošević T, Podlogar M, Bdikin I, Irurueta GO, Hortigüela MJ, Gonçalves G (2021) Graphene-based TiO_2 nanocomposite for photocatalytic degradation of dyes in aqueous solution under solar-like radiation. *Appl Sci* 11:3966-3980 <https://doi.org/10.3390/app11093966>

22. Krishnan S, Murugesan S, Vasanthakumar V, Priyadharsan A, Alsawalha M, Alomayri T, Yuan B (2020) Facile green synthesis of $\text{ZnFe}_2\text{O}_4/\text{rGO}$ nanohybrids and evaluation of its photocatalytic degradation of organic pollutant, photo antibacterial and cytotoxicity activities. *Colloids Surf A Physicochem Eng Asp* 611: 125835-125870 <https://doi.org/10.1016/j.colsurfa.2020.125835>
23. Kumar K V, Chakra CHS (2017) Synthesis and structural characterization of ZnCr_2O_4 nanoparticles prepared by citrate-gel auto combustion method. *Asian J Phys Chem Sci* 2:1-7 DOI: 10.9734/AJOPACS/2017/34683
24. Kumar S, Kaushik RD, Upadhyay GK, Purohit LP (2021) rGO-ZnO nanocomposites as efficient photocatalyst for degradation of 4-BP and DEP using high temperature refluxing method in in-situ condition. *J Hazard Mater* 406:124300 <https://doi.org/10.1016/j.jhazmat.2020.124300>
25. Nafiey AL, Kumar A, Kumar M, Addad A, Sieber B, Szunerits S, Boukherroub R, Jain SL (2017) Nickel oxide nanoparticles grafted on reduced graphene oxide (rGO/NiO) as efficient photocatalyst for reduction of nitro aromatics under visible light irradiation. *J Photochem Photobiol A Chem* 336:198-207 <https://doi.org/10.1016/j.jphotochem.2016.12.023>
26. Naz S, Durrani SK, Mehmood M, Nadeem M (2016) Hydrothermal synthesis, structural and impedance studies of nanocrystalline zinc chromite spinel oxide material. *J Saudi Chem Soc* 20: 585-593 <https://doi.org/10.1016/j.jscs.2014.12.007>
27. Nguyen MA, Zahran EM, Wilbon AS, Besmer AV, Cendan VJ, Ranson WA, Lawrence RL, Cohn JL, Bachas LG, Knecht MR (2016) Converting light energy to chemical energy: A new catalytic approach for sustainable environmental remediation. *ACS Omega* 1:41–51, <http://dx.doi.org/10.1021/acsomega.6b00076>
28. Ollis DF, Pelizzetti E, Serpone N (1991) Photocatalyzed destruction of water contaminants. *Environ Sci Technol* 25:1522–1529. doi:10.1021/es00021a001
29. Padhi DK, Panigrahi TK, Parida K, Singh SK, Mishra PM (2017) Green synthesis of $\text{Fe}_3\text{O}_4/\text{RGO}$ nanocomposite with enhanced photocatalytic performance for Cr (VI) reduction, phenol degradation, and antibacterial activity. *ACS Sustain Chem Eng* 5:10551–10562 <https://doi.org/10.1021/acssuschemeng.7b02548>
30. Palanisamy G, Pazhanivel T, Bhuvaneswari K, Bharathi G, Marimuthu G, Maiyalagan T (2020) Spinel oxide ZnCr_2O_4 incorporated with ZnS quantum dots for application on visible light driven photocatalyst Azo dye degradation. *Colloids Surf A Physicochem Eng Asp* 590: 124505-124536 <https://doi.org/10.1016/j.colsurfa.2020.124505>
31. Peng C, Gao L (2008) Optical and photocatalytic properties of spinel ZnCr_2O_4 nanoparticles synthesized by a hydrothermal route. *J Am Ceram Soc* 91:2388–2390 DOI: 10.1111/j.1551-2916.2008.02417.x
32. Pokhrel S, Jeyaraj B, Nagaraja KS (2003) Humidity-sensing properties of $\text{ZnCr}_2\text{O}_4\text{--ZnO}$ composites *Mater Lett* 57:3543–3548 [https://doi.org/10.1016/S0167-577X\(03\)00122-8](https://doi.org/10.1016/S0167-577X(03)00122-8)
33. Qian R, Zong H, Schneider J, Zhou G, Zhao T, Li Y, Yang J, Bahnemann DW, Pan JH (2018) Charge carrier trapping, recombination and transfer during TiO_2 photocatalysis: An overview. *Catal Today* 335:78-90 <https://doi.org/10.1016/j.cattod.2018.10.053>
34. Rahaman AB, Sarkar A, Singha T, Chakraborty K, Dutta S, Pal T, Ghosh S, Datta PK, Banerjee D (2020) Electrical transport properties and ultrafast optical nonlinearity of rGO–metal chalcogenide ensembles.

35. Sabet M, Jahangiri H (2018) The effects of surfactant on the structure of ZnCr_2O_4 dendrimer like nanostructures used in degradation of Eriochrome Black T. *Mater Res Express* 5:015035 <https://doi.org/10.1088/2053-1591/aaa442>
36. Salehi M, Eshaghi A, Tajizadegan H (2018) Synthesis and characterization of $\text{TiO}_2/\text{ZnCr}_2\text{O}_4$ core-shell structure and its photocatalytic and antibacterial activity. *J Alloys Compd* 778:148-155 <https://doi.org/10.1016/j.jallcom.2018.11.025>
37. Sen MB, Ghosh S (2017) Enhanced sunlight photocatalytic activity of silver nanoparticles decorated on reduced graphene oxide sheet. *Korean J Chem Eng* 34:2079-2085 <https://doi.org/10.1007/s11814-017-0090-5>
38. Shang J, Hao W, Lv X, Wang T, Wang X, Du Y, Dou S, Xie T, Wang D, Wang J (2014) Bismuth oxybromide with reasonable photocatalytic reduction activity under visible light. *ACS Catal* 4:954–961 <https://doi.org/10.1021/cs401025u>
39. Sharma N, Sharma V, Jain Y, Kumari M, Gupta R, Sharma SK, Sachdev K (2017) Synthesis and characterization of graphene oxide (GO) and reduced graphene oxide (rGO) for gas sensing application. *Macromol Symp* 376:1700006-1700010 <https://doi.org/10.1002/masy.201700006>
40. Singh PK, Kuo KY, Lee JT, Hsiao PH, Juan JC, Duong HP, Chen CY (2021) Synergistic absorbents based on $\text{SnFe}_2\text{O}_4/\text{ZnO}$ nanoparticles decorated with reduced graphene oxide for highly efficient dye adsorption at room temperature. *RSC Adv* 11:17840–17848 DOI: 10.1039/d1ra02317a
41. Sudesh, Kumar N, Das S, Bernhard C, Varma GD (2013) Effect of graphene oxide doping on superconducting properties of bulk MgB_2 . *Supercond Sci Technol* 26:095008-095015 <http://dx.doi.org/10.1088/0953-2048/26/9/095008>
42. Tajizadegan H, Heidary A, Torabi O, Golabgir MH, Jamshidi A (2016) Synthesis and characterization of ZnCr_2O_4 nanospinel prepared via homogeneous precipitation using urea hydrolysis. *Int J Appl Ceram Technol* 13:289–294 <https://doi.org/10.1111/ijac.12440>
43. Tantubay K, Das P, Sen MB, (2020) Ternary reduced graphene oxide– CuO/ZnO nanocomposite as a recyclable catalyst with enhanced reducing capability *J Environ Chem Eng* 8:103818–103824 <https://doi.org/10.1016/j.jece.2020.103818>
44. Thennarasu G, Sivasamy A (2015) Synthesis and characterization of nanolayered $\text{ZnO}/\text{ZnCr}_2\text{O}_4$ metal oxide composites and its photocatalytic activity under visible light irradiation. *J Chem Technol Biotechnol* 90: 514–524 DOI 10.1002/jctb.4343
45. Wang Y, An T, Yan N, Yan Z, Zhao B, Zhao F (2020) Nanochromates MCr_2O_4 ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$): Preparation, characterization, and catalytic activity on the thermal decomposition of fine AP and CL-20. *ACS Omega* 5:327–333 <http://dx.doi.org/10.1021/acsomega.9b02742>
46. William S, Hummers J, Offeman RE (1958) Preparation of graphitic oxide. *J Am Chem Soc* 80:1339 <https://doi.org/10.1021/ja01539a017>
47. Wong CC, Chu W (2003) The hydrogen peroxide-assisted photocatalytic degradation of alachlor in TiO_2 suspensions. *Environ Sci Technol* 37:2310-2316 <https://doi.org/10.1021/es020898n>

48. Yu L, Wang L, Sun X, Ye D (2017) Enhanced photocatalytic activity of rGO/TiO₂ for the decomposition of formaldehyde under visible light irradiation. J Environ Sci 73:138-146 DOI: 10.1016/j.jes.2018.01.022
49. Zanatta AR (2019) Revisiting the optical bandgap of semiconductors and the proposal of a unified methodology to its determination. Sci Rep 9(11225):1–12

Figures

Figure 1

a XRD pattern and b FTIR spectra of ZnCr2O4 NPs and ZnCr2O4-rGO nanocomposite

Figure 2

a UV-Vis absorbance spectra ZnCr2O4-rGO nanocomposite b Tauc's plot

Figure 3

FESEM images of a ZnCr₂O₄ and b ZnCr₂O₄-rGO, c and d TEM and HRTEM images of ZnCr₂O₄-rGO, e particle distribution graph of ZnCr₂O₄-rGO nanocomposite f EDX of ZnCr₂O₄-rGO nanocomposite

Figure 4

a photocatalytic degradation efficiency b plot of $\ln(A_0/A_t)$ Vs. time c PL spectra of ZnCr₂O₄ NPs and ZnCr₂O₄-rGO nanocomposite

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [scheme1.png](#)
- [scheme2.png](#)
- [SupportingInformation.docx](#)