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Catalytic activity of graphene oxide hybridized $ZnWO_4$ for dyes degradation and oxidation of functionalized benzyl alcohols

Abstract

A simple sol-gel method was used to prepare the GO hybridized $ZnWO_4$ nanoparticles (NPs). The size and morphology of prepared GO/$ZnWO_4$ NPs can be controlled by adjusting the reaction time and temperature. The NPs were characterized using XRD, FTIR and UV-DRS to study their optical properties. The resultant sample is a phase pure GO/$ZnWO_4$ was confirmed by XRD. As-prepared GO/$ZnWO_4$ shows band gap energy of 2.32eV, which shown a path to study the catalytic studies i.e. dyes degradation and oxidation of functionalized benzyl alcohols. The obtained results declared the prepared GO/$ZnWO_4$ NPs have better catalytic efficiency in dyes degradation of Caramine Indigo (CI) and Crystal Violet (CV) under visible-light illumination.

Keywords: GO/$ZnWO_4$, sol-gel, caramine indigo, crystal violet, 2-chloro benzyl alcohol, 4-hydroxy benzyl alcohol, 4-hydroxy 3-methoxy benzyl alcohol, 3-nitro benzyl alcohol and 3,4-dimethoxybenzyl alcohol

Volume 2 Issue 5 - 2018

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Received: August 06, 2018 | **Published:** October 29, 2018

Introduction

Recently, nanomaterials have great attention due to their unique size, shape, and crystallinity dependent optical, electronic, magnetic and chemical properties.[1] Metal tungstates such as. Bi_2WO_6, $CdWO_4$, $PbWO_4$, $MnWO_4$ and $FeWO_4$ are inorganic functional nanomaterials and widely used in scintillators materials, sensors, magnetic devices, photocatlaytic and magnetism field.[2] Among them, $ZnWO_4$ has a great potential in photocatalytic degradation of organic dye pollutants under UV light illumination.[2–3] But, the efficiency is very low because of sunlight captures only 5% while visible light captures the 35%. Hence, this material activity brings to visible region by doping of ions, form hybrids or composites with graphene or CNT. Graphene is a sp2 hybridized carbon with zero band gap energy and has specific physicochemicoelectrical properties thus it shows excellent applications in photocatalysis and organic conversions.[4] There have been persistent efforts to load photocatalysts on the structure of graphene oxide (GO) to enhance the photo catalytic activity, but few studies have focused on the surface coating by GO on the photcatalyst for enhancing the photo catalytic efficiency and producing visible photocatalytic activity.

In order to enhance the sensitivity of photocatalyst, $ZnWO_4$ controlled by tuning morphologies, controlling crystallinity and ion doping, or to explore the photoelectrocatalytic activities. The dye pollutants such as 4-chlorophenol, Methylene blue, Rhodamine B, Phenol, Crystal violet, Caramine indigo, Salicylic acid, Methyl orange and Acetaldehyde under visible light irradiation were degraded by $ZnWO_4$ have been reported earlier.[2,5] For instance, synthesized $ZnWO_4$ nanorods doped with cadmium ions successfully by a hydrothermal method for the photocatalytic degradation of rhodamine B in aqueous solution which showed that cadmium ions doping also greatly improved the photocatalytic efficiency of $ZnWO_4$ nanorods.[6] Recently, reported the several $ZnWO_4$-based composites of high UV light photocatalytic activities via hydrothermal, microwave and co-precipitation methods.[7] The sol-gel technique has been used to synthesize metal tungstate nanocomposites especially in the fabrication of self-cleaning film and glass coating due to require a low synthesis temperature, the physical properties of the doping component could be retained by controlling the mixture between the guest molecule and the host matrices.[8]

To the best of our knowledge, this is the first report on visible light photoactivity of graphene oxide hybridized $ZnWO_4$. Herein, a simple and facile route to synthesize the visible-light responsive GO hybridized $ZnWO_4$ NPs was developed. Furthermore, the catalytic activity was examined for dyes degradation and benzyl alcohol oxidation.

Experimental section

Materials and methods

Zinc Nitrate ($Zn(NO_3)_2.4H_2O$), sodium tungstate ($Na_2WO_4.2H_2O$), ethylene glycol, Graphite flakes, sodium nitrate ($NaNO_3$), sulphuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl) and potassium permanganate ($KMnO_4$) were procured from Sigma Aldrich, India and used without further purification. Milli Q water was used in whole experiment.

Synthesis of Graphene Oxide (GO)

The preparation of graphene oxide (GO) was carried out by unique modified Hummer's method.[4] In a typical synthesis, 1g of graphite flakes was added into 2.5g of $NaNO_3$ and 100mL of concentrated H_2SO_4 under stirring. Then, 3g of $KMnO_4$ was added gradually to this mixture at 10°C under stirring for 2h. The resulting mixture was added to 100mL of distilled water and then heated to 98°C. The obtained mixture was continued to be stirred for 2h. After that, 10mL of H_2O_2 was added in the mixture with stirring for 2h. The colour of the mixture changed to bright yellow. Finally, the mixture was filtered and washed with a 5% HCl aqueous solution to remove metal ions, followed by distilled water for removal of the acid. The resulting solid with brown black colour was separated by ultrasonic treatment in water and dried at 60°C for 12h.

Synthesis of ZnWO$_4$

In a typical experiment, Nanoparticles of ZnWO$_4$ were prepared by dissolving 0.05mmol of Zn(NO$_3$)$_2$.4H$_2$O and 0.05mmol of Na$_2$WO$_4$.2H$_2$O was dissolved separately in ethylene glycol (EG) under continuous stirring. After complete dissolution, the two mixtures were stirred at constant temperature for 24h, and cooled to room temperature. Excess of sodium was removed by washing with distilled water and finally with absolute ethanol. The precipitate thus formed was dried at 70°C and calcinated at 300°C.[2]

Synthesis of GO hybridized ZnWO$_4$

A certain amount of GO was dispersed in water, then exfoliation of GO was achieved by ultrasonicating the dispersion for 60min. The obtained brown dispersion was then subjected to centrifugation to remove the unexfoliated GO. The obtained exfoliated GO was then dispersed in 100mL ethylene glycol, and the as-prepared ZnWO$_4$ was added into the dispersion and dispersed by ultrasonication for 30min and stirred for 48h. In a typical procedure, and ammonia solution (28wt% in water) were added to the above dispersion. After being vigorously stirred for a few minutes, the dispersion was put into a water bath (90°C) for 3h. An opaque powder was obtained after evaporation at 60°C for 12h. GO/ZnWO composites with different mass ratios ranging from 1% and 2% were prepared according to this method. Amongst the composites, 2% shows the phase and photocatalytic activity.

Characterization

The formation of pure phase was confirmed by XRD (Bruker-6000) with Cu KR radiation (λ) 0.154178nm). The functional groups were identified using FTIR (IR prestige 21) and band gap was calculated using UV-DRS (Shimadzu 2600R) spectra was taken from 200-800cm^{-1} with BaSO$_4$ as reference. The photocatalytic test was carried out using UV-visible spectrophotometer (Shimadzu 2600) by taking spectra from 200 to 800cm^{-1}.

Photocatalytic activity

The prepared NPs were tested for photocatalytic activity towards degradation of two model dyes under visible-light illumination. Initially, 0.1g of prepared catalyst was added to 20mg/L of dye solution and stirred for 30minutes to attain adsorption-desorption thermal equilibrium. After that, the dye solution was irradiated to visible light which is source from metal halide lamp. For every half an hour, collected the aliquots and centrifuged to separate the catalyst. Finally, the solution was studied the photocatalytic activity by UV-visible spectrophotometer. The degradation efficiency was calculated using the following equation.

$$\text{Photo degradation } \% = \frac{C_0 - C_t}{C_0} \times 100$$

Where C_0 and C_t corresponds to the initial absorbance and absorbance at time‘t’ respectively.

Results and discussion

Characterization techniques

X-ray diffraction (XRD) analysis: The XRD patterns of GO/ZnWO$_4$ are shown in Figure 1. The GO/ZnWO$_4$ sample should present a two-phase composition of GO and ZnWO$_4$ and compared with standard JCPDS file (No.88-0251). No impurity phase was observed, which is evident in the GO/ZnWO$_4$ NPs. Notably, no typical diffraction peak belonging to the separate GO is observed in the GO/ZnWO$_4$ nanocomposites. The reason is that the main characteristic peak of graphene at 24.5° might be shielded by the main peak of ZnWO$_4$, which is at 24.5° and indexed to (110) crystal planes. Figure 2 (ESI) shows the XRD patterns of GO which exhibits a (001) plane reflection at 2θ=9.12° is contributed to a basal spacing of d_{001}=0.961nm.[4,9] Based on this, the interlayer spacing of GO was calculated to be 0.961nm. This value is higher than interlayer spacing of graphite flakes (d-spacing= 0.334nm, 2θ=26.4°), due to the presence of oxygenated functional groups and intercalated water molecules. The average crystalline size of prepared NPs was calculated using Debye-Scherrer equation.

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

Where λ is the wavelength at angle θ of inclined plane. The calculated crystalline size of GO/ZnWO$_4$ is 18.3nm which is lower than ZnWO$_4$ (29.6nm). This is due to that the incorporation of ZnWO$_4$ onto GO sheets.

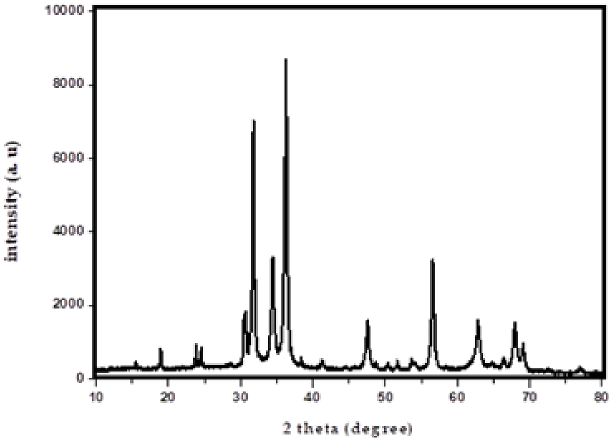

Figure 1 XRD spectrum of GO/ZnWO$_4$.

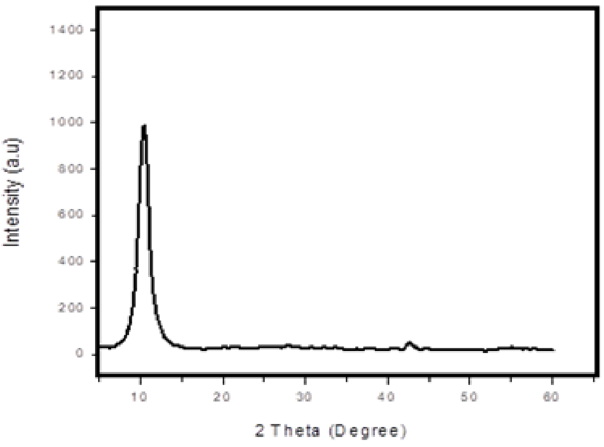

Figure 2 FTIR spectrum of GO.

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FTIR: FT-IR spectrum of the GO is shown in Figure 3 (ESI). The presence of different types of oxygen functionalities in GO were confirmed at broad and wide peak at 3447cm^{-1} which is attributed to O-H stretching vibrations of the C-OH groups and water.[4,9] The absorption peaks at 1560cm^{-1} can be ascribed to benzene rings. The sharp intense peak at 1419cm^{-1} can be attributed to CO group.[7]

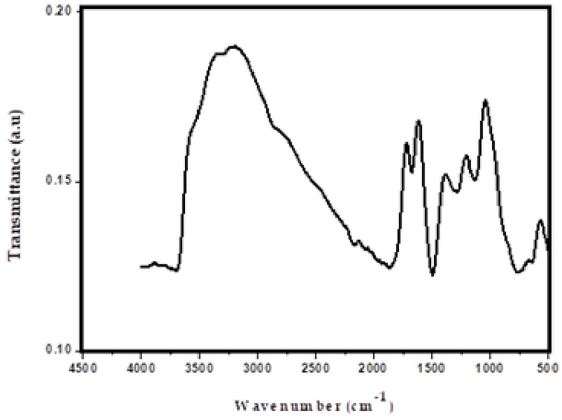

Figure 3 XRD spectrum of GO.

FTIR spectrum of GO/$ZnWO_4$ is shown Figure 4. The vibrational peaks of GO are consistent with fingerprint groups such as carboxylic species, hydroxyl species, and epoxy species (C=O, 1734cm^{-1} OH deformation, 1400cm^{-1} the C−OH stretching, 1230cm^{-1} C−O−C stretching, 1061cm^{-1} skeletal ring stretch, 1624cm^{-1}). The absorption peak at around 1580cm^{-1} clearly shows the skeletal vibration of the GO sheets, indicating the formation of a graphene structure.[4] The two peaks at 3447 and 1629cm^{-1} observed for ZnWO^4 implies the existence of basic hydroxyl groups in the $ZnWO_4$ sample. These results clearly indicate that the surface of $ZnWO_4$ is hydroxylated. Another peak was observed at 1385cm^{-1} results from the O-H absorption of hydrogen-related defects. The peak at 1385cm^{-1} decreased and the peak at 1230cm^{-1} (C−OH) is slightly observed for GO/$ZnWO_4$, indicating that defect sites may be occupied by graphene. The broad peak is located at 907cm^{-1}, corresponding to the stretching W−O mode. Thus, a supposition could be proposed that the GO and $ZnWO_4$ are chemically bonded.

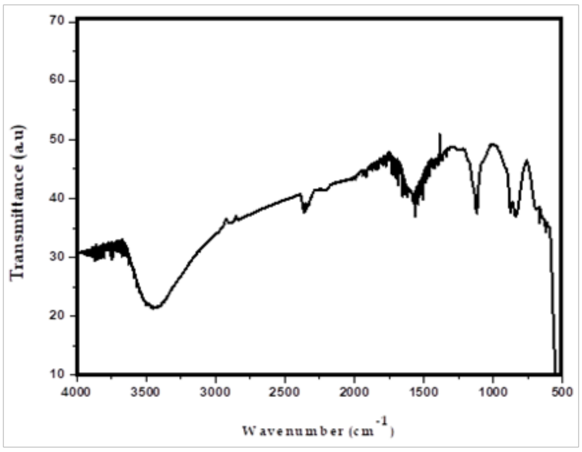

Figure 4 FTIR spectrum of GO/$ZnWO_4$.

UV-Visible Diffuse reflectance spectra: UV-Vis DRS was performed between 200 to 800nm range and $BaSO_4$ was used as a reference. Spectral grade $BaSO_4$ was taken as reference for the reflectance spectra Photoabsorptive ability of the sample is assessed by UV-DRS shown in Figure 5. UV-DRS show an absorption edge in the region close to 550nm from which the estimated band gap of the synthesized GO/$ZnWO_4$ powder is calculated to be 2.32eV, suggested that it is apt to captures the visible-light when compared to pure $ZnWO_4$ (3.2eV) which is fall in UV region.[2]

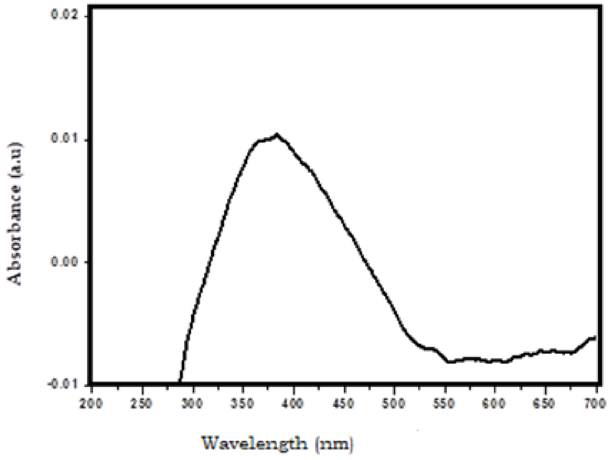

Figure 5 UV DRS spectrum of GO/$ZnWO_4$.

Catalytic activity applications

Photocatalytic degradation of dyes

The photocatalytic activity of GO/$ZnWO_4$ NPs was tested via degradation of aqueous solutions of dyes, CI and CV under Visible light irradiation at similar conditions (catalyst dose is 0.1g, pH is 9.5 and concentration is 20mg/L of dye solutions). Figures (6 & 7) show the photocatalytic degradation of CI and CV at different time intervals with decreasing intensity of peaks. The complete degradation was taken in 150min for CI and 120min for CV under visible light irradiation by synthesized GO/$ZnWO_4$. This result was strongly supported by the UV-DRS spectrum and indicated the band gap energy of GO/$ZnWO_4$ was 2.3eV. There is no change observed in the degradation of CI and CV in the absence of catalyst after continuous irradiation of visible light for 3h. The rate constants of the degrading process also calculated as shown in Figure 8, which indicates that entire process follows the pseudo first order reaction. The linear relationship between ln (C/C_0) and time demonstrates pseudo-first-order kinetics.

$$\eta = \ln (C/C_0) = kt$$

Where C/C_0 is normalized CI and CV concentrations, t is the reaction time, and k is the reaction rate constant (min^{-1}).

Mechanism

The basic principle of the photocatalysis can be described by water splitting technology.[1,4,9] As the light is absorbed by the $ZnWO_4$, the electrons are emitted from valence band (VB), leaving a hole behind and this electron enters into conduction band (CB) while the light has equal or higher photon energy than the band gap of the material. Reduction of the H^+ ions to H_2 occurs by the electrons in the CB, while the oxidation of H_2O to O_2 occurs by the holes in the VB. GO

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was irradiated with light, then it releases electrons into CB of ZnWO$_4$ (Eqs 1-5). A possible mechanism was explained in Figure 9. Catalysts with smaller band gaps can absorb the light in higher wavelengths and thus active in a larger part of the solar spectrum. Therefore, finding the material which has a smaller band gap is one of the main concerns.

$$ZnWO_4 + h\upsilon \rightarrow ZnWO_4\left(e^- + h^+\right) \text{-----------} \qquad \text{Eq (1)}$$

$$GO + h\upsilon \rightarrow e^- \text{---------------------------} \qquad \text{Eq(2)}$$

$$e^-_{CB} + O_2 \rightarrow {}^{\bullet}O_2^- \text{-----------------------} \qquad \text{Eq(3)}$$

$$ZnWO_4\left(h^+\right) + OH \rightarrow {}^{\bullet}OH \text{ --------------} \qquad \text{Eq(4)}$$

$${}^{\bullet}OH + {}^{\bullet}O_2 + NB \rightarrow CO_2 + H_2O \text{-------------} \qquad \text{Eq(5)}$$

Evaluation of oxidation capacity of GO/ZnWO$_4$

GO/ZnWO$_4$ NPs assemblies were used for benzyl alcohol oxidation as a catalyst. In the reaction mixture, 0.5mL of substituted benzyl alcohol was added with 25mL of acetonitrile (as solvent) in a round bottomed flask. Then, 100mg of GO/ZnWO$_4$ powder and 3mL of 30% H$_2$O$_2$ solution were introduced into the mixture and heated at 70°C for about 12h as shown in Figure 10. The flask was fitted with aluminium foil to avoid the impinging of atmospheric oxygen. A usual almond smell represents the formation of benzaldehyde, which stipulates the completion of reaction. After completion of the reaction, the products were purified and recrystallized with methanol.[2,10] The final products were further confirmed by ^{1}H NMR, FT-IR, and ^{13}C NMR studies

Spectral data of 4-hydroxy 3-methoxybenzaldehyde

IR (KBr pellet) : 3300 cm^{-1}, 3100cm^{-1}, 1660cm^{-1}, 1600cm^{-1}, 1100cm^{-1} ^{1}H NMR (400MHz/CDCl$_3$) δppm : 7.17(1H,d), 7.32(1H,s), 6.72 (1H, d), 9.87 (1H, s), 3.62 (1H, s) ^{13}C NMR (22.5 MHz/CDCl$_3$) δppm : 189.2, 149.2, 148.3, 130.1, 117.2, 116.7, 55.5 Mass-ESI: 151 (M).

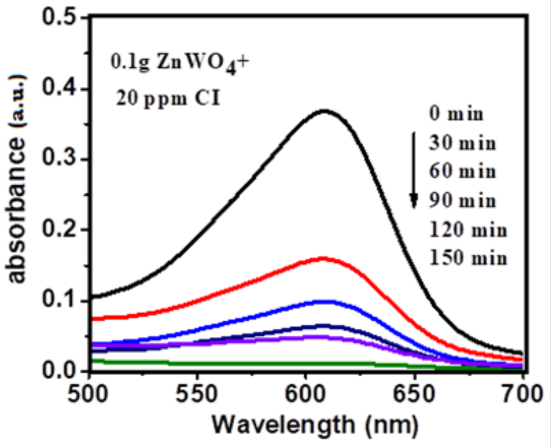

Figure 6 Photocatalytic degradation of CI using GO/ZnWO$_4$ under visible light irradiation.

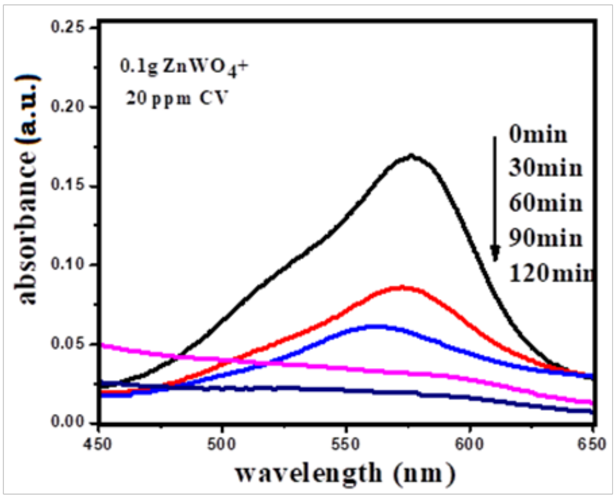

Figure 7 Photocatalytic degradation of CV using GO/ZnWO4 under visible light irradiation.

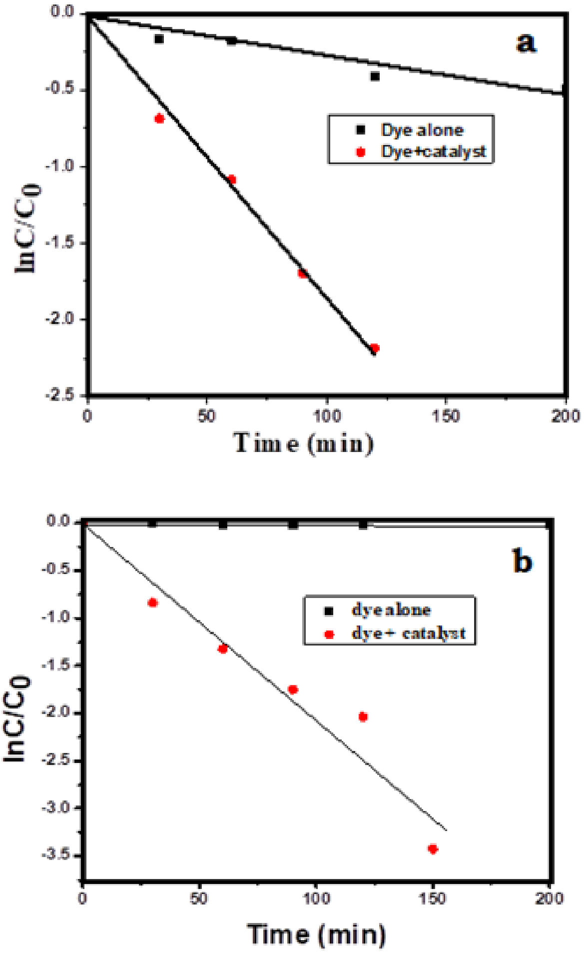

Figure 8 Rate constants of (c) CI (d) CV using GO/ZnWO4 under visible light irradiation.

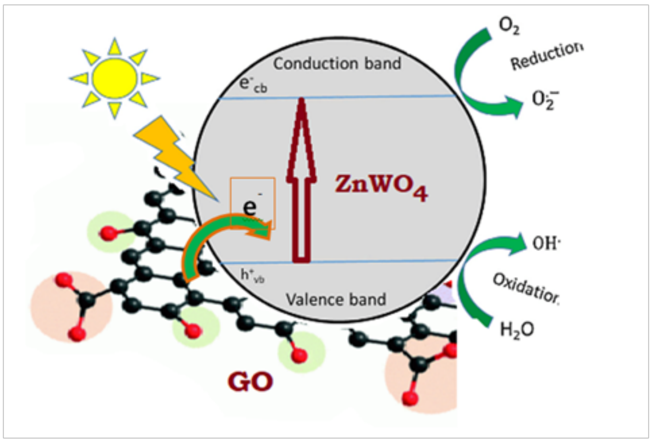

Figure 9 Possible mechanism of photocatalytic degradation of dyes.

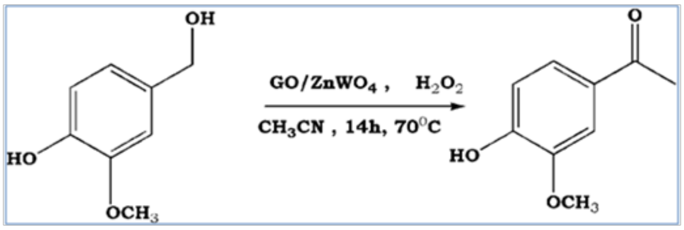

Figure 10 Benzyl alcohol oxidation using $GO/ZnWO_4$.

Conclusion

The $GO/ZnWO_4$ NPs were synthesized by sol-gel approach. The photocatalytic activity of $GO/ZnWO_4$ NPs were evaluated by testing the photo degradation of model dyes like caramine indigo and crystal violet under visible light irradiation. This result indicated that the complete degradation of 100mL aqueous solutions of 20ppm CI and CV under visible light irradiation in 150 and 180min respectively. Also, synthesized $GO/ZnWO_4$ NPs are apt to the synthesis of benzaldehydes under solvent-free conditions with good yield.

Acknowledgements

None.

Conflict of interest

Authors declare that there is no conflict of interest.

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