



Modified ZnO for Efficient Photo-Catalysis by Silver/Graphite oxide Nanoparticles

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Abstract

ZnO was modified with ternary composites Ag:ZnO/GO to enhance the interaction/reaction activities by simple evaporation/ photo-deposition of Graphite oxide and Silver respectively. The ternary composites were characterized by analysis the structure or morphology with X-ray diffraction, UV-visible diffraction to find band gap and surface area S_{BET} . The process include change in sequence of preparations which tested by removing Eosin yellow by adsorption and photocatalytic degradation. The results shows that ZnO after modifications was more active then pristine phase and Ag :(ZnO/GO) was more activities then (Ag:ZnO)/GO in photo-reaction but less abilities in adsorption.

Keywords: Eosin Yellow, Ternary composites, Ag: ZnO/GO, Degradation.

Introduction

ZnO as nanomaterials are commonly known such amazing species for photocatalysts reaction due to all literatures related that for cost and safety with stability [1]. Another literatures Highlights towards the abilities to use ZnO in many applications such photocatalytic degradation, a gas sensor, electronic and optoelectronic devices and antimicrobial activity [2-3]. The diversity or verity in shape and size starting from 0D to 3D with many methods for synthesis may be all of this can decided or suppose the mechanism of pristine ZnO activity [3].

The issue will inevitably differ for ZnO in composite which reported experimentally for many research in this field [4] not for change in activity but due to appearing new properties. The style used to preparing binary or ternary composites influence directly in the activity which related to number of active site that could be work in the reaction. In other words the binary composite consist of two materials, the nature of loading or connection between the support and loading species affect by the

method of preparation. This work ternary composites Ag: ZnO/GO were prepared by

using photo-deposition/simple impregnation method and characterized by X-ray diffraction, UV-visible diffraction and surface area. The activities of synthesized materials were tested by adsorption/photo-degradation of Eosin Yellow.

Experimental

Materials

Eosin yellow (EY) from Merck/ Germany was used as pollutant in this work which behave the physicochemical properties. The graphite was purchased from Fluke; silver nitrate ($AgNO_3$) salt was supplied by Sigma-Aldrich and Hydrogen peroxide (30%) from Barcelona-Spain. Ammonium hydroxide. 37% was supplied from Sigma Aldrich.

Synthesis of Ternary Composites

At first Graphite was oxidation by modifying piranha reagent as we reported in our previous work [5] briefly 1 g of graphite was

dispersion in 30 ml of H₂O₂/NH₄OH (1:1) with stirring for 3 hours at 10 °C. The byproduct was drying at 80 °C for 4 hours, than used to synthesize ternary composites.

Two types of binary composite were prepared: ZnO/GO and Ag: ZnO by a simple evaporation and photo deposition method respectively [6].

Ag was deposited onto ZnO by photo-deposition method when mixture of 50% aqueous ethanol solution with required amount of AgNO₃ was irradiation by 1.3 m W of VU-light. The deposition was accrued with irradiated for 6 hour at 40°C, using a 200-W mercury lamp to produce 5%Ag: ZnO which mention in first section of figure 1 Ag: ZnO. The second sections include Firstly oxidations for graphite G to graphite oxide GO. Graphite 200mg was treated with 80 ml

of H₂O₂/H₂SO₄ (1:1) with stirring for 1hours which repeated three times then washing and thermal treatments at 100°C to forming graphite oxide GO.

The required amount of GO was dispersed in 200 ml of distilled water using ultra-sonic water bath for 30 min with gradually adding ZnO powder. The suspension was washing and drying at 100°C for 6 hours to produces ZnO/5%GO which mentions in second section by ZnO/GO in figure 1. The first binary composites Ag:ZnO was impregnated GO with the same ratios of Ag by a simple evaporation to forming (Ag:ZnO)/GO. The second ternary composites were prepared by phot-deposition of Ag into ZnO/GO with the same conditions which mentions previously to forming Ag :(ZnO/GO).

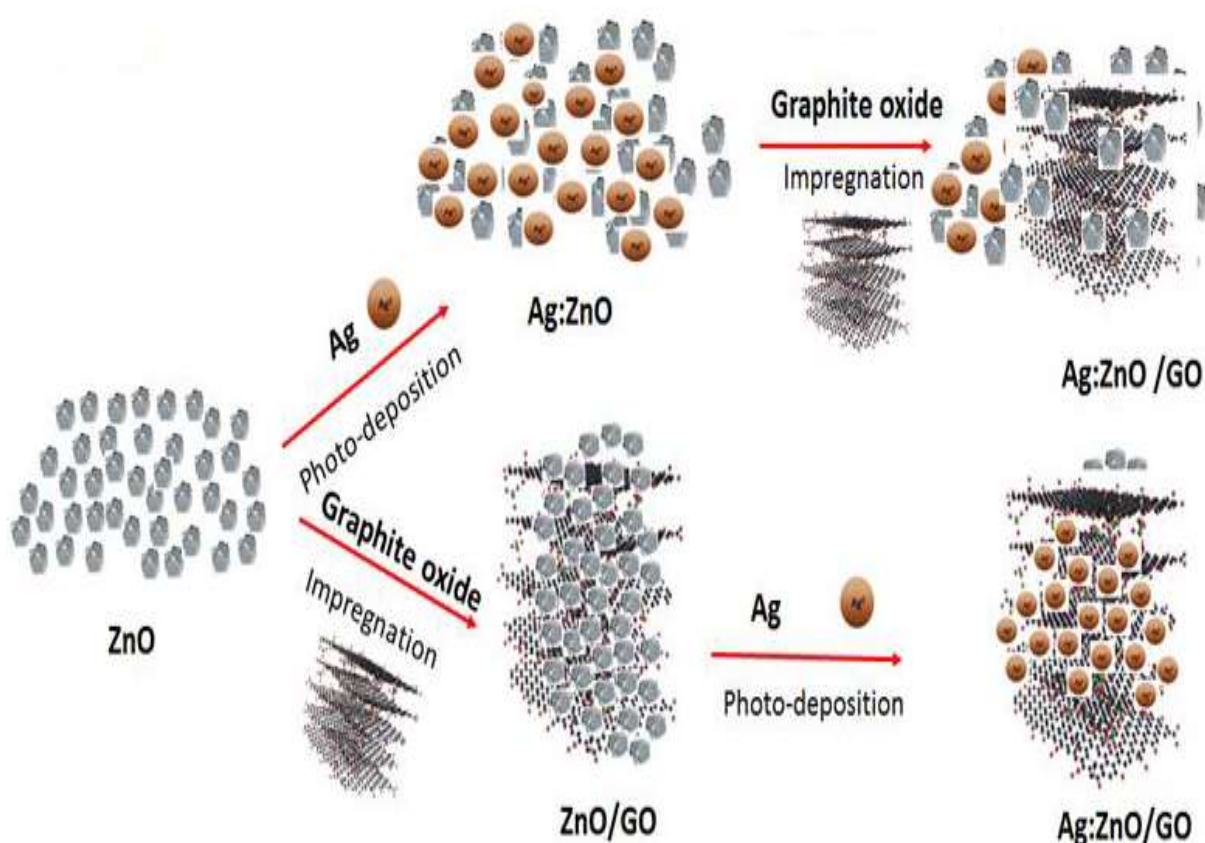


Figure 1: Scheme for the steps of synthesized binary and ternary composites by photo-deposition and a simple evaporation methods

Reaction System

The Eosin yellow EY was used as pollutant for the adsorption/photo-degradation process by using pristine and modified ZnO in ternary composites. The concentration of EYs was 60 ppm and the natural PH was 6 at 298

K with light intensity 1.3 mW cm⁻² that used in experiments and magnetically stirred at 475 rpm in the dark and light reaction. The adsorption or dark reaction were done to find the equilibrium time of adsorption which was equal to 2 h. Figure 2 refer to the reaction which include 200 mg of catalyst which

dispersed in 100 mL of 60 ppm EYs in 250 mL Pyrex glass reservoir. The reaction were studies by taken sample every 30 min which cleaned by centrifuge then analyzed from

300-700 nm using a UV-vis spectrophotometer at maximum wave length 515 nm.

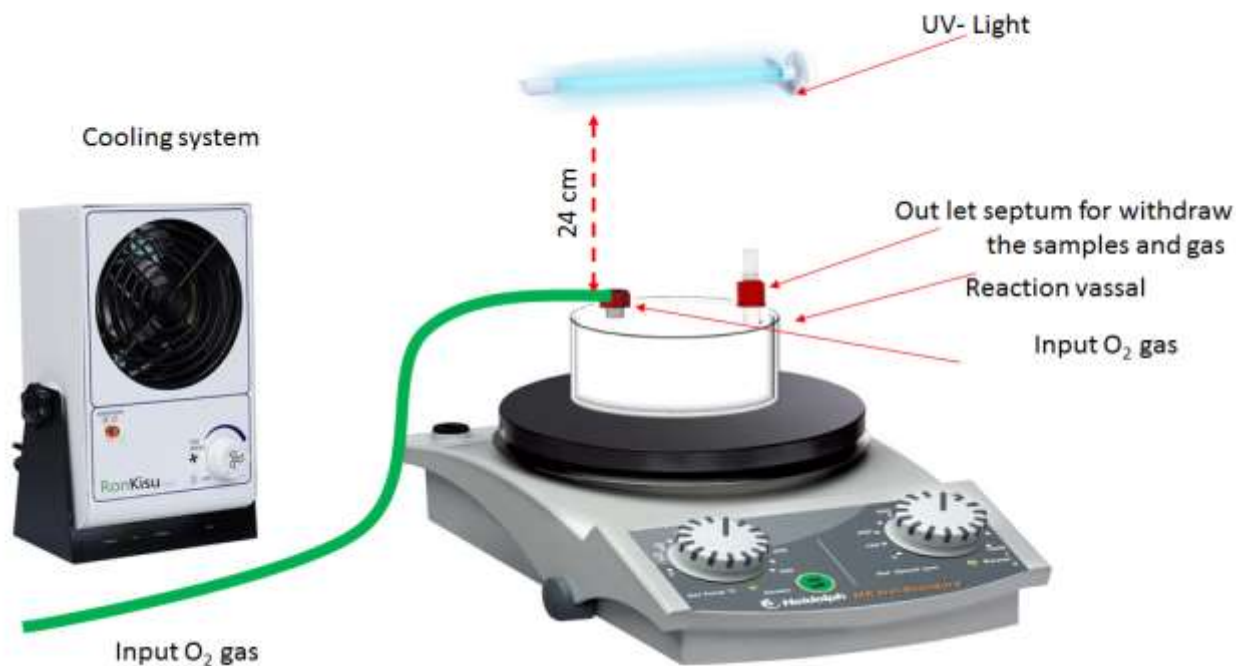


Figure 2: skim for the reaction system that used in adsorption interaction and photo-catalytic degradation reaction

Characterization

The prepared samples were characterized by X-ray diffraction, UV-visible reflectance and surface area S_{BET} . The X-ray diffraction (XRD) patterns were done as reported in our previous work [7] by a (Riga Rotaflex) (RU-200B) X-ray diffractometer using for the 2θ

between 10 and 80° and a scan rate of 5°/min. The change in band gap energy of before/after modification ZnO in ternary composites was measured diffuse reflectance spectroscopy (DRS) within the 200–700 nm spectrum by a UV-vis spectrophotometer (Varian Cary 100). The surface area for the samples were measured using Micrometric Auto MATE 23.

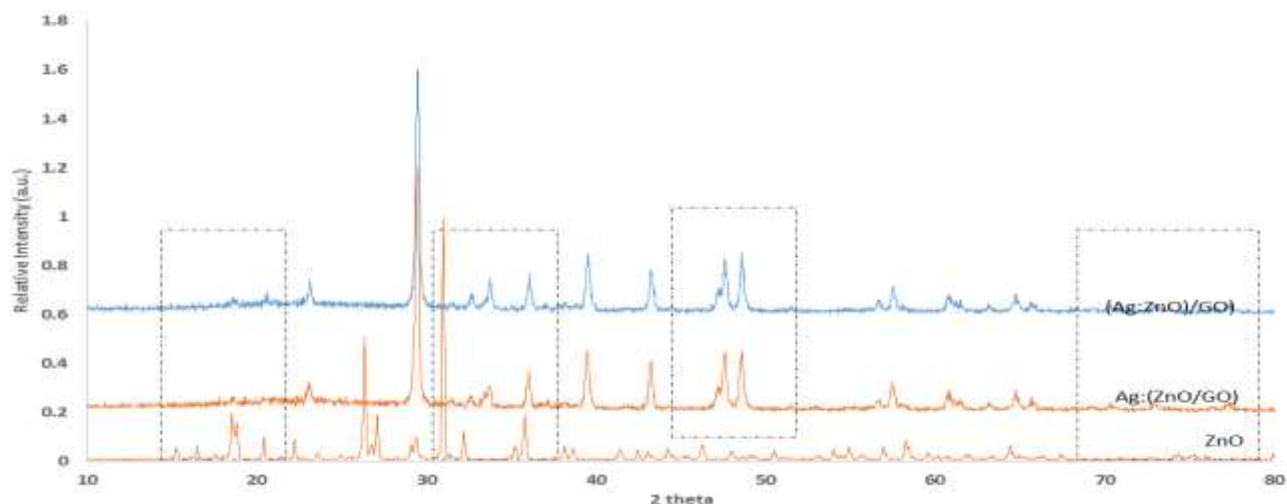


Figure 3: XRD patterns for pristine and modified ZnO in ternary composites [Ag:(ZnO)/GO, (Ag:ZnO)/GO]

Figure 3 shows the XRD spectrum of materials when the peaks 33.8° (100), 36.7° (002), 38° (101), 48° (102), 56.5° (110), and

66.2° (112) can be related to ZnO, while 44° (111), 47° (200) and 63.3° (103) for cubic phase Ag [1].

The peaks which related to Ag refer to forming Ag nanoparticles by photo-deposition onto ZnO and ZnO/GO without any Ag oxide

species. The large peak at 29° can be due to graphite oxide [8] which appeared with Ag :(ZnO/GO) and (Ag:ZnO)/GO.

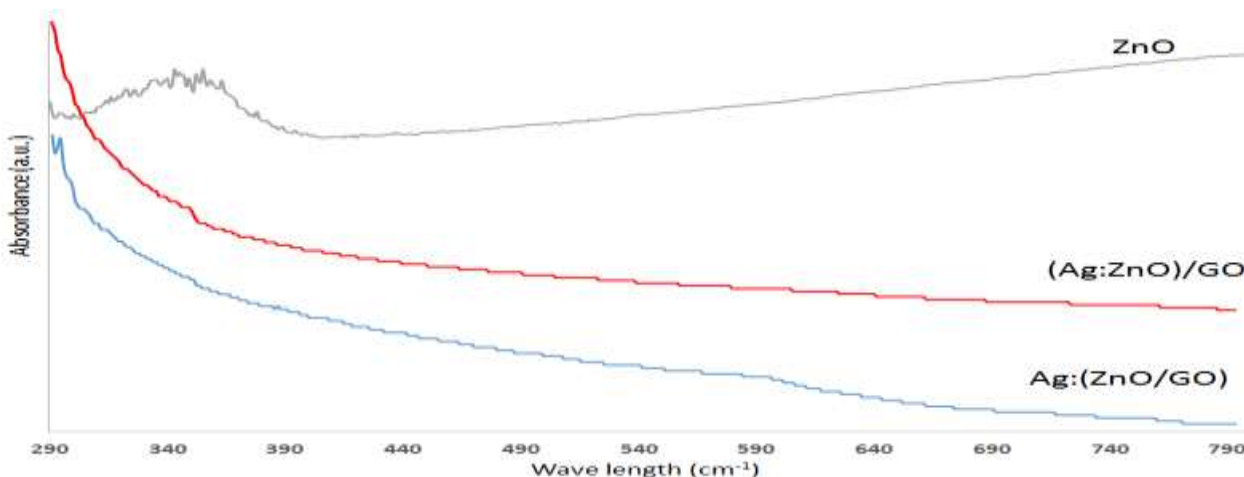


Figure 4: UV-visible spectra of absorbance for ZnO, Ag :(ZnO/GO) and (Ag:ZnO/GO) from 290-790 nm

The UV-vis absorption spectra of pristine ZnO and modified in ternary composites: Ag/rGO, ZnO/rGO and pristine ZnO are presented in figure 4. The photo-absorption activity of ZnO was showed in 375 nm while the two ternary composites shows new activity in 585 nm which is more clear with Ag :(ZnO/GO) in addition to the primary activity.

active with light and more conductivities causing reduce in band gap for the ternary groups. These behaviors were agreed with Moss-Burstein effects thus increase the exciting electrons due to forming new oxygen vacancies in new structure [10].

The absorbance spectra refer increase the activities with light after modified ZnO which is more active with Ag:(ZnO/GO) due to appears new peaks in 585 nm which is in visible part of light [9]. The ZnO before doping with Ag or impregnating with GO the absorbance of light was limited with specific region which is UV. After impregnated onto GO and doping with Ag, ternary composites shows new behavior when change positively due to addition new materials which is more

The Activity of Ternary and Pristine ZnO

The activities of pristine ZnO and ternary composites with 3% GO and Ag firstly tested with abilities for adsorption EYs before photo degradation. The results of adsorptions were plotted in figure 5 which shows the change in adsorption interaction between the catalyst with different constrictions and EYs. Figure vv shows the adsorption of 60 ppm by 200 mg by pristine and modifies ZnO in ternary and binary composites with the variance in sequence of preparation as the arrangement below:(Ag:ZnO)/GO > Ag :(ZnO/GO) > ZnO

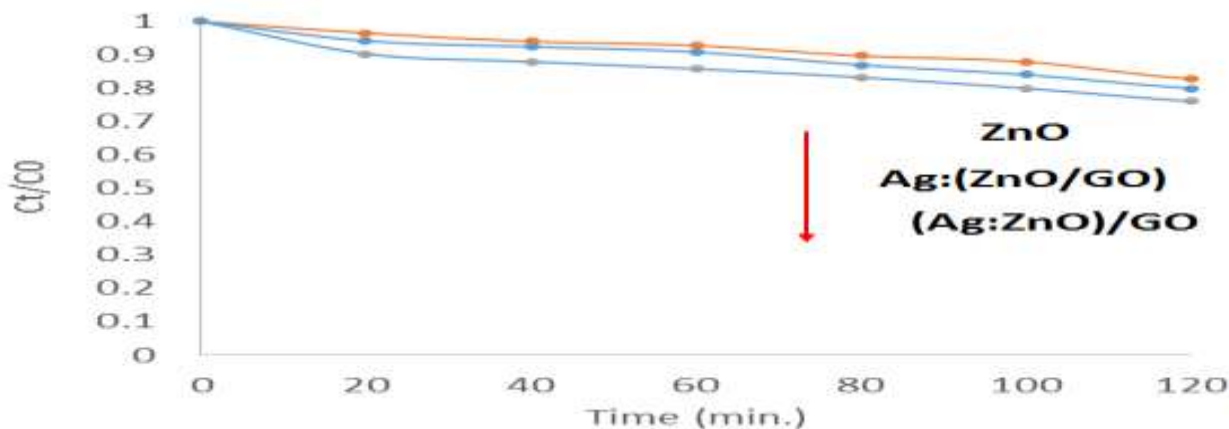


Figure 5: the change in Ct/C0 with the time for adsorption process of 60 ppm Eosin Yellow by ZnO, Ag:(ZnO/GO) and (Ag:ZnO)/GO at 25°C

Figure 6, reported The activity towards photocatalytic degradation were shown two behavior: the first, ternary composites were more active than ZnO while The second Ag:(ZnO/GO) was more then (Ag:ZnO)/GO although the adsorption for the first was less than the other.

The changes on the concentrations of EYs (C_t/C_0) with time were account for the extent of photocatalytic-dicolorazation by the catalysts in Figure 6. The value of C_t/C_0 with time for adsorption /photocatalytic reaction showed that change the activity between

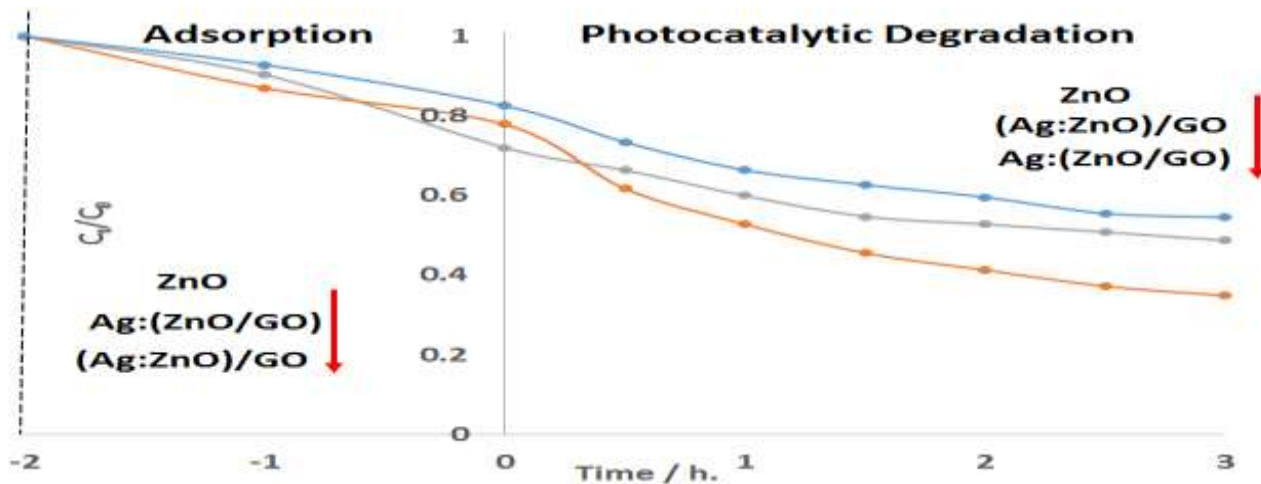


Figure 6: the change in C_t/C_0 with the time for remove of 60 ppm Eosin Yellow by adsorption/photocatalytic degradation process by ZnO, Ag:(ZnO/GO) and (Ag:ZnO)/GO at 25°C

Figure 7 refer to the kinetic studies for photocatalytic degradations which were tested for pseudo first and second order of the linear forms as shown in equation 1 and 2 respectively.

$$\ln(C_0/C_t) = k_1 t \quad \dots\dots\dots 1$$

$$1/C_t = k_2 t + 1/C_a \quad \dots\dots\dots 2$$

The experimental data were plotted in figure 888 which applying to calculate rate constants k_1 and k_2 derived from the slopes and the correlation coefficients R^2 from intercepts. The results of R^2 and value of degradation rate k were listed in table 333, which behave pseudo second order with Ag:(ZnO/GO) while with pristine ZnO and Ag:(ZnO/GO) were did not shows clear variance.

Table 1: summary of R^2 and k for the probabilities of the first and second order photocatalytic degradation by pristine and modified ZnO

sample	Pseudo first order		Pseudo second order	
	R^2	k_1	R^2	k_2
ZnO	0.973	0.0014	0.980	0.233
(Ag:ZnO)/GO	0.924	0.00180	0.985	0.267
Ag:(ZnO/GO)	0.808	0.0026	0.996	0.570

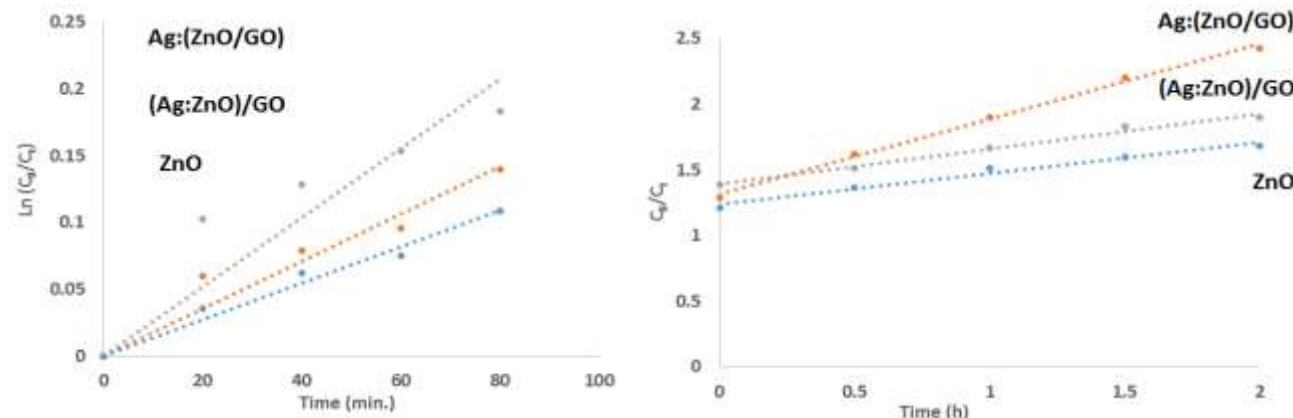


Figure 7: Compare the k values calculated according to the first and second order reaction for photocatalytic-degradation of Eosin Yellow with 200 mg ZnO, Ag:(ZnO/GO) and (Ag:ZnO)/GO

The efficiency of interaction and reactions with adsorption and photo-catalytic degradations between EYs and ZnO in pristine and modified phase were represent in

Figure 8. The efficiency was represent by percentage of removal %R which reported in Table 2 with two activities.

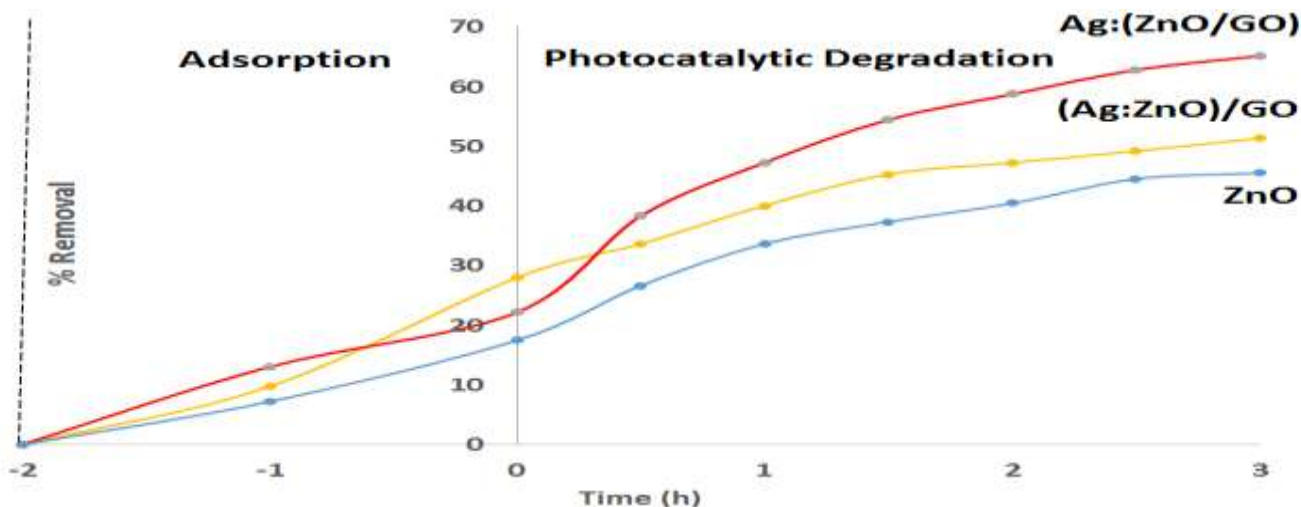


Figure 8: Removal percentage of EYs by ZnO and two types of ternary composites Ag:(ZnO/GO) and (Ag:ZnO)/GO by Adsorption and Photocatalytic degradation at 25°C

The ratios of removal for the adsorption and degradation of EYs by ZnO, Ag:(ZnO/GO) and

(Ag:ZnO)/GO were listed in table 2, when reported the removal with different activities.

Table 2: the ratios of removal percent of EYs by ZnO, Ag:(ZnO/GO) and (Ag:ZnO)/GO

Catalyst	%R (Adso.)	%R (Photo-deg.)	Total %R
ZnO	17.5	28	45.5
(Ag:ZnO)/GO	28.1	23.3	51.4
Ag:(ZnO/GO)	22.2	43	65.2

The results of adsorptions can be related to created many active sites from GO that able to interaction with EYs when succeed to distribution out of the matrix. The second ternary composites Ag:(ZnO/GO) mostly Ag species were covered the binary composites ZnO/GO during photo-deposition which reduces many active sites that could be adsorbed EYs. Band gap for ZnO was 3.3 e V [11] while Band gap for graphite oxide GO

was reported less than 2 e V [12]. The photo-excited electron e- transfer electrons into the CB of ZnO react with O₂ molecules forming dissolved O₂^{•-}, leaving h⁺ active towards forming OH[•] from H₂O [13]. The both species react with EYs causing dicolorazation then degradation with the time with specific activity depending on the band gap, light intensity, concentration of solutions, and ether parameters that influence onto to activity e-/h⁺ which decided the efficiency [14].

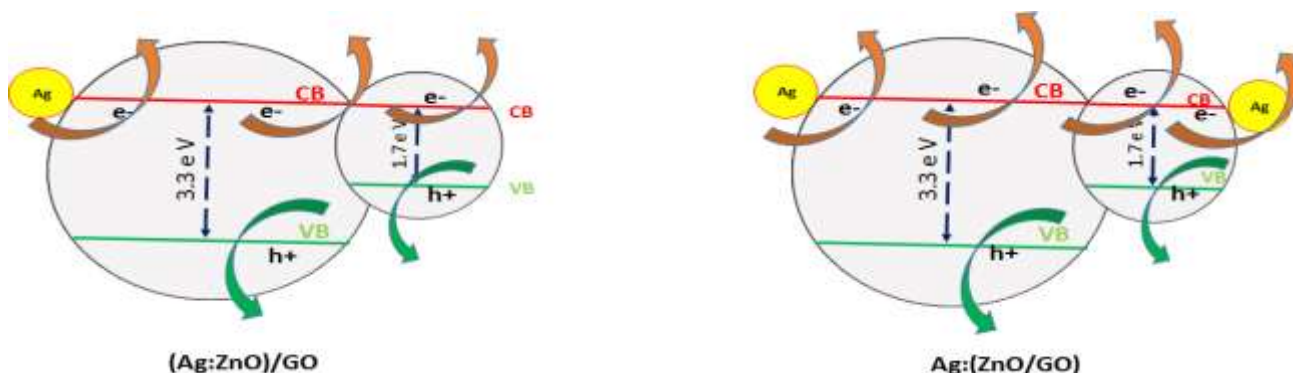


Figure 9: the skin of the transfer mechanism for photocatalytic degradation of (Ag:ZnO)/GO and Ag:(ZnO/GO)

The Mechanism of the Reaction

The Fermi level of Go or Ag is higher than that of ZnO, which prefer the transfer of electrons from GO or/ and Ag to ZnO to reach stable with less energy for new Fermi energy. When the Ag:(ZnO/GO) and (Ag: ZnO)/GO nanocomposites are illuminated under UV light which is the same sources of ZnO, electrons in VB were excited to CB, forming h^+ in VB. the CB of ZnO is higher than the new stable modified Fermi energy level of two types of ternary composites, thus the ratios of electrons that able to react with EYs were less as compare with two ternary composites.

The second case when the same conditions were applied with Ag:ZnO/GO the new modified fermi level which is less band then the last were succeed to forming more and more excited e-/h+. The ZnO in ternary composites was more active not for lower Fermi level but also Ag and GO forming new bridge to moving the electrons towards outside of Ag:ZnO/GO with higher conductivity.

The results were agreed with our previous work [15, 6] when mentions before the additions materials to semiconductor in ternary composite create new ways to moving the electrons towards new activities with different ways. One of the most important ways were explained in figure 9, when higher photo induced electrons can transfer from the CB of ZnO with different sequence to the GO and Ag causing reduce the e-/h+ recombination. The third cases about the evaluate the efficiency for the two types of ternary composites Ag:(ZnO/GO) and (Ag:ZnO)/GO include two part S_{BET} and absorbance or band gap. The surface area for

ZnO was 5.3 m²/g while for the two types were 29 m²/g and 56 m²/g respectively may be able to explain the adsorption abilities for (Ag:ZnO)/GO compare Ag:(ZnO/GO) . The evaluate photocatalytic activity of Ag :(ZnO/GO) and (Ag:ZnO)/GO nanocomposites can be related to many reasons. The first: conductivity of Ag was more than GO thus real and direct contact between ZnO and Ag mostly enhance reducing in Fermi level.

The second: photo deposition of Ag after impregnated ZnO into Go reduce the agglomerates due to dispersion Ag into more surface area and that raise the active sites more than the first case. The third: the delocalized and orientations the Ag and GO gropes with ZnO with the ideal or at least reduce losing the active sites thus in figure nnn, many four way to transfer the e- as compare to three ways. The four ways were represent by surface of ZnO, transfer the e- to Ag or GO, and transfer the e- from/to Ag and GO which deposited onto GO.

Conclusion

Pristine ZnO were modified by impregnated with GO and doping Ag which done by change the sequence of preparation when doping/firstly or impregnated than complete the process. The results showed that the morphology and conductivity with surface area were variant when change the sequence of preparations. The variant appeared in new and different activities in spite of include the ternary composites the same ratios of continents. However the activities change due to all the parameters which mentions above influence in sensitivity and selectivity towards adsorption or photo catalytic degradation.

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